CHAPTER 1
INTRODUCTION

1.1 Rare Earth Elements

The Rare Earth Elements, or lanthanides, as they are generally known, are a group of 15 elements that have similar ionic radii and valency state and belong to Group IIIA of the Periodic Table. Scandium and Yttrium are also some times considered as a part of REE. REE are usually denoted as Heavy Rare Earth Elements (HREE) and Light Rare Earth Elements (LREE), based on their atomic weights. Lanthanum, cerium, praseodymium, neodymium, promethium, samarium and europium are grouped as LREE. Gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium are generally considered the HREE. The term Middle REE (MREE) is sometimes used to refer those elements between europium and dysprosium (Samson and Wood, 2004). The HREE group is particularly important to emerging technologies in green energy, defence and electronic industries (Humphries, 2010; Long et al., 2010; British Geological Survey, 2011; Kato et al., 2011).

The relative abundance of REE varies considerably and relates to two main factors. It has been observed that REE with even atomic number have greater abundance than their odd numbered neighbours (Oddo-Harkins effect) and secondly the lighter REE are more incompatible (owing to their larger ionic radii) and consequently are more concentrated in the continental crust than the REE with higher atomic numbers. The chemically similar nature of REE allows them to substitute for one another resulting in the occurrence of multiple REE in one mineral and a broad distribution in the earth'scrust (Caster and Hedrick, 2006). For example, in Bastnaesite, cerium is the dominant REE, but it also contains lanthanum, praseodymium and neodymium. The vast majority of the resources are associated with just three minerals; bastnaesite, monazite and xenotime. In some REE minerals LREE are particularly enriched compared to HREE, whilst in others the opposite is the case. Bastnaesite and monazite are the primary sources of LREE mainly Ce, La and Nd. Xenotime is dominated by heavier REE including Dy, Er, Yb, and Ho (Harben, 2002). Promethium undergoes radioactive decay (half-life is 2.62 years) and, therefore, its presence in the natural environment is virtually none. Yttrium (Y) is another element that generally occurs in close association with REE because of its chemical similarity and geochemical affinity, eventhough it is not a member of the REE.

The REE are a coherent group of elements in that all the different elements show very similar chemical behaviour. They are highly electropositive and their compounds are generally ionic in character. They form oxides, halides, carbonates, phosphates and silicates. Their ionic radii are relatively large and so substitution reactions usually involve the large cations such as calcium or strontium. REE have decreasing crystal ionic radii from La (1.016 Å) to Lu (0.85 Å) (Piper and Bau, 2013). They are mainly trivalent, with the exception of Ce and Eu, which are also stable in the tetra and divalent oxidation states. The valance difference in Eu and Ce result in chemical reaction differences of these two elements with rest of the 3^+ REE. The decreasing ionic radii from La to Lu cause different fractionation patterns in various phases during geochemical processes (Henderson, (1984)). Table 1.1 shows some selected properties of REE.

The arrangement of electrons around the nuclei of the different REE is a determination factor of the properties of these elements. Ground state electronic configurations of REE have at least one electron in the 4f orbital, while the outer 5d shell remains empty, except in gadolinium, lanthanum and lutetium which have an electron in the 5d shell. In their oxidised state the elements have no electrons in their outer 5d shell and any changes in the number of electrons being reflected in the inner 4f level. It is a fact that the change in the electronic configuration in the different rare earths is mostly confined to the inner shells

Table 1.1: Selected Properties of REE

(Compiled from Gupta and Krishnamurthy (2005)).

Element	Symbol	Atomic Number	Atomic Weight	Density (gcm^3)	Melting Point (^0C)
Lanthanum	La	57	138.90	6.146	918
Cerium	Ce	58	140.11	8.160	798
Praseodymium	Pr	59	140.90	6.773	931
Neodymium	Nd	60	144.24	7.008	1021
Promethium	Pm	61	145.00	7.264	1042
Samarium	Sm	62	150.36	7.520	1074
Europium	Eu	63	151.96	5.244	822
Gadolinium	Gd	64	157.25	7.901	1313
Terbium	Tb	65	158.92	8.230	1356
Dysprosium	Dy	66	162.50	8.551	1412
Holmium	Ho	67	164.93	8.795	1474
Erbium	Er	68	167.26	9.066	1529
Thulium	Tm	69	168.93	9.321	1545
Ytterbium	Yb	70	173.04	6.966	819
Lutetium	Lu	71	174.97	9.841	1663

rather than the outer ones that gives these elements their coherence in chemical behaviour. Europium has a ground state electronic configuration ([Xe] $4f^7 6s^2$) with a half-filled f orbital, allowing stability for the Eu^{2+} species. Similarly ground state electronic configuration of Ce ([Xe] $4f^1 5d^1 6s^2$) permits either Ce^{3+}or Ce^{4+}, with electron configurations corresponding to [Xe]$4f^1$ and [Xe], respectively.

Consideration of the size of trivalent REE in six-fold coordination shows that only a few other ions in the same coordination have sizes between that of the largest La^{3+} (10.32 nm) and the smallest, Lu^{3+} (8.61nm). These include Na^+ (10.2 nm), Ca^{2+} (10.00 nm) and Y^{3+} (9.0 nm). Examples of ions smaller than Lu are Zr^{4+}

(7.2 nm) and Hf^{4+} (7.1 nm). Any geochemical behaviour that is significantly depend on ionic radius, such as partitioning between different coexisting minerals, will tend to reflect the variation of ionic radius of the REE.

1.2 Crustal Abundance

The term REE is a misnomer as these elements are relatively plentiful in the Earth's crust having an overall crustal abundance of 9.2 mg. kg^{-1}(Rudnic et al. 2005). The crustal abundance of individual REE varies widely from cerium, the most abundant at 43 mg. kg^{-1} to Thulium at 0.28 mg. kg^{-1}(Tayler and Mclennan, 1985). The most abundant rare-earth elements after cerium are lanthanum and neodymium. Seven of the REE have abundances between 1 and 10 mg. kg^{-1} comparable with those of other important economic elements such as tungsten, tin, arsenic and bromine. Four of the REE have abundance between 15 and 100 mg. kg^{-1} similar to that of copper, cobalt, rubidium and zinc. In general, the REE show decrease in abundance with increase in atomic number. Promethium is virtually absent in the crust since it has no naturally occurring stable or lon g-lived isotope (Jones, *et al*., 1996).

Table 1.2 shows the Crustal abundance estimated by different authors for REE. The abundance of REE oscillates with atomic number and so normalising the concentration of REE in a rock is found very useful to compare their geochemistry. Normalisation eliminates the abundance variation between lanthanides of odd and even atomic number and allows determination of the extent of fractionation between the lanthanides, because such fractionation is not considered to have taken place during chondrite formation.

The concentration of individual REE is normalised to its abundance in chondrites by dividing the concentration of the given element in the rock by the concentration of the same element in chondritic meteorites (Kimoto et al., 2005).

Table1.2: Crustal abundances of REE in mg. kg^{-1} (After Jones et al, 1996).

Element	Weaver and Tarney(1984)	Taylor and McLennan (1985)		Shaw et al. (1986)	Condie (1993)	
		Upper Crust	Bulk Continental Crust		Mao Model	Restoration Model
Y	13	22	20	21	29	30
La	27	30	16	32.3	25.6	27.3
Ce	55	64	33	65.6	55.7	59.3
Pr	--	7.1	3.9	--	--	--
Nd	23	26	16	25.9	24.6	26.6
Sm	3.9	4.5	3.5	4.51	5.04	5.43
Eu	1.07	0.88	1.1	0.937	1.02	1.01
Gd	--	3.8	3.3	2.79	4.81	5.11
Tb	0.50	0.64	0.60	0.481	0.76	0.80
Dy	--	3.5	3.7	--	--	--
Ho	--	0.80	0.78	0.623	--	--
Er	--	2.3	2.2	--	--	--
Tm	0.23	0.33	0.32	--	--	--
Yb	1.46	2.2	2.2	1.47	2.33	2.36
Lu	--	0.32	0.30	0.233	0.43	0.43

This normalisation smoothes out the concentration variations from element to element and helps in comparing the REE content in different rocks. Chondrites are used for this purpose because they are primitive solar material which may have been the parental material of the earth. Table 1.3 shows the abundance of the REE in a composite sample of 12 chondrites and in North American Shales Composite (NASC) and Post Archaean Australian Shale (PAAS).

Table 1.3: REE abundance of Chondrites, North American Shale Composites (NASC) and Post Archaean Australian Shale (PAAS).

Element	Abundance (mg. kg^{-1})		
	12 chondrites[1]	NASC[2]	PAAS[3]
La	0.34	32	38.2
Ce	0.91	73	79.6
Pr	0.121	7.9	8.83
Nd	0.64	33	33.9
Sm	0.195	5.7	5.55
Eu	0.073	1.24	1.08
Gd	0.26	5.2	4.66
Tb	0.047	0.85	0.774
Dy	0.30	-	4.68
Ho	0.078	1.04	0.991
Er	0.2	3.4	2.85
Tm	0.032	0.5	0.405
Yb	0.22	3.1	2.82
Lu	0.034	0.48	0.433

[1]Wakita, Rey and Schmitt (1971).[2] Haskin et al. (1968).[3] Schmidt et al. (1963).

1.3 Major Classes of REE Deposits

The rare earths occur only as trace elements in majority of sedimentary, igneous or metamorphic rocks. They will tend to concentrate in several rock forming minerals including titanite, apatite, zircon, epidote, garnet and clays. The concentration and distribution of REE in mineral deposits is influenced by rock forming and hydrothermal processes including enrichment in magmatic or hydrothermal fluids, separation into mineral phases and precipitation and subsequent redistribution and concentration through weathering and other surface processes (British Geological Survey, 2011). Environments in which REE are enriched can be broadly divided into two categories: (i) primary deposits associated with igneous and hydrothermal processes and (ii) secondary deposits concentrated by sedimentary processes and weathering.

1.3.1 Primary Deposits

The REE are preferentially enriched in partial melts of fluids from upper mantle and in melts of crustal origin because of their large ionic radius (Moller, 1986). The economic potential of a REE deposit is strongly influenced by its mineralogy and geological processes from which it has formed. Deposits which have a spatial and genetic association with alkaline igneous rocks can be divided into two categories, one associated with carbonatites and related igneous rocks and the other with peralkaline igneous rocks (Samson and Wood, 2004). Descriptions of various types of REE deposits can be found in Neary and Highley (1984), Mariano (1989a&b), Wall and Mariano (1996), Castor and Hedrick (2006), Castor (2008), and Long et al., (2010). Orris and Grauch (2002) provide a worldwide compilation of data on rare earth mines, deposits, and occurrences. Studies by Nesbit (1979) and Duddy (1980) have shown that granodiorite and volcanic rocks weathered in humid and warm climate were transformed into clay minerals such as kaolinite, halloysite and montmorillonite. Rare earth minerals such as bastnasite and gadolinite present in these rocks also get weathered releasing rare earth ions to form RE aqua and RE hydroxyl ions adsorbed on clay minerals resulting in the formation of RE ores in China as suggested by Prudencio et al (1993).

1.3.1.1 Deposits associated with Carbonatites

Carbonatites are defined by the International Union of Geological Sciences (IUGS) system of igneous rock classification as having more than 50 modal percent primary carbonate minerals, such as calcite, dolomite, and ankerite, and less than 20 percent SiO_2 (Le Maitre, 2002). Carbonatites have high abundances of Sr, Ba, Pand LREE (Nelson et al. 1988).They have been subdivided on the basis of their dominant modal carbonate mineral, such as calcite, or dolomitecarbonatites and on their corresponding major element geochemistry with Mg-, Ca, Fe- and REE-carbonatites (Woolley 1982; Le Bas 1987; Woolley and Kempe 1989).Carbonatites can be quite diverse and are likely to originate from multiple processes (Woolley, 2003; Mitchell, 2005).They originate from carbon dioxide rich and silica poor magmas from the upper mantle. Carbonatites take a variety of forms including intrusions within alkali complexes, isolated dykes and sills, small plugs or irregular masses that may not be associated with other alkaline rocks. Carbonatites are enriched in a range of elements in addition to carbon dioxide, calcium, magnesium and iron, including REE, barium, strontium, fluorine, phosphorus, niobium, uranium and thorium (Rankin, 2004).

The REE in carbonatites are almost entirely LREE which occur in minerals such as bastnasite, allanite, apatite and monazite (Gupta and Krishnamurthy, 2005). REE deposits are also associated with late-stage vein and replacement mineralisation either within carbonatites or surrounding host rocks. Carbonatites are mostly intrusive and extrusive bodies are rare. The carbonatite volcano in northern Tanzania is an example of extrusive carbonatite body (Woolley and Church, 2005). Mineral deposits associated with carbonatites account for the greatest production of REEs. Important deposits are the Bayan Obo deposit in Inner Mongolia (China), and the Sulphide Queen Carbonatite of the Mountain Pass district, California.

1.3.1.2 Deposits associated with Alkaline Igneous rocks

Carbonatite and alkaline intrusive complexes, as well as their weathering products, are the primary sources of REE (Long *et al*., 2010). Alkaline rocks are deficient in SiO_2 relative to Na_2O, K_2O, and CaO (Winter, 2001). Alkaline intrusive rocks tend to be spatially associated with carbonatites and contain elevated concentrations of REE. Alkaline rocks can be further classified based on their chemistry. Peralkaline rocks are one subset of alkaline rocks, defined by $(Na_2O + K_2O)/(Al2O_3)>1$, and they commonly are enriched in REE.

Although there are no alkaline intrusion-related deposits currently being mined for REE, many are in various stages of exploration because these peralkaline igneous rocks contain relatively high concentrations of heavy REE. Carbonatite and alkaline intrusion-related REE deposits tend to be enriched in high field strength elements (REE, Y, Nb, Zr, and U). REE-rich alkaline intrusion-related deposits have variable REE enrichments, but are not as enriched in LREE as carbonatites (Verplanck et al. 2014).

Carbonatites and peralkaline igneous rocks associated with REE deposits tend to occur within stable continental tectonic units, in areas defined as shields, cratons, and crystalline blocks; they are generally associated with intracontinental rift and fault systems (Berger *et al.*, 2009). These igneous rocks formed from the cooling of silica-under saturated, alkaline magmas, which were derived by small degrees of partial melting of rocks in the Earth's mantle. The evolution of these initial mantle melts to form REE mineral deposits is not fully understood. The source of REE is the initial magma, and with decreasing pressure and temperature the magma evolves, which leads to further enrichments in REE. Crystallization is one process that drives the evolution of the magma.

In general, REE deposits associated with peralkaline intrusive complexes fall into two categories: (1) deposits in peralkaline, layered complexes, and (2) deposits in veins or dikes associated with peralkaline intrusions (Verplanck et al. 2014). A variety of REE-bearing minerals are associated with alkaline intrusion-related REE deposits, in part because secondary processes tend to overprint the primary mineralogy. Important REE-bearing mineral phases include apatite, eudialyte, loparite, gittinsite, xenotime, gadolinite, monazite, bastnäsite, kainosite, mosandrite, britholite, allanite, and zircon.

1.3.2 Secondary Deposits

1.3.2.1 Placer Deposits

Weathering of terrigenous rock releases resistant and dense minerals, which by the action of natural agencies such as rivers, winds etc., get enriched to form placer deposits. The placer deposits often contain economically valuable minerals. Minerals which are resistant to chemical and physical weathering are generally accumulated in placer deposits. The weathering resistance and exceptional density of monazite and xenotime help them to concentrate in placer deposits as part of the heavy-mineral assemblage (Carleton et al. 2016). The important placer deposits of the world are mostly of marine origin and are found along the present or palaeo-shorelines. The heavy minerals (HM) in these deposits are concentrated by wave action, tides and currents. During 1980s monazite and xenotime produced from titania-zircon beach placers in Australia were one of the most important sources of REE. A very little REE production is currently derived from monazite-bearing placers owing to their typically high thorium content and associated high levels of radio activity (Caster and Hedrick, 2006). Australian placer deposits have local concentrations up to 1 per cent monazite and Indian ilmenite placer deposits can contain 1-2 per cent monazite (Moller, 1986).

1.3.2.2 Residual Weathering Deposits

Laterites and lateritic bauxites are the most important residual formations in the tropical areas. They are the products of intense subaerial rock weathering. Lateritization processes are the consequence of an environment in which the metals Al, Mg, Fe, Cu, Ni and REE are totally or partially freed from their parent rock minerals and then accumulate in the laterite-saprolite weathering profile (Morteani and Preinfalk, 1996). The Lateritization process dramatically changes the mineralogical and chemical composition of the primary rock. Investigations of weathering profiles indicate that REE mobility and deposition in surface environments are distinctly influenced by changes in the ground water pH conditions. In deeper part of the laterite and to a lesser extent in the saprolite, secondary phosphates are formed and adsorb most of the REE. Ion adsorption clays associated with weathered REE-enriched granites, occur throughout southern China. They are particularly rich in heavier REE and have extremely low content of radioactive elements (Chi and Tian, 2008).

Most rocks found at the surface of the earth may have been affected by weathering. Unless the weathering is very intense, the pattern of abundance for the REE may not show any major change (Martin et al., 1978, Mysen, 1978). Most of the igneous rocks that have undergone essentially static metamorphism or only very limited hydrothermal alteration or weathering should give REE patterns and abundances indicative of the original rock.

1.4 REE in offshore Area

Japanese scientists have found vast reserves of rare earth metals on the Pacific seabed that can be mined cheaply, a discovery that may break the Chinese monopoly on a crucial raw material needed in hi-tech industries and advanced weapons systems. The team of scientists from Japan's Agency for Marine-Earth Science and the University of Tokyo first discovered huge reserves in the mid-Pacific two years ago. These are now thought to be 1000 times all land-based deposits, some of it in French waters around Tahiti. The latest discovery is in Japan's Exclusive Economic Zone in deep-sea mud around the island of Minami-Torishima at 5,700 meters below sea level. Uptake of rare earth elements by mineral phases such as hydrothermal iron-oxyhydroxides and phillipsite seems to be responsible for their high concentration. The rare-earth elements and yttrium are readily recovered from the mud by simple acid leaching, and suggest that deep-sea mud constitutes a highly promising resource for these elements (Kato et al., 2011).

Seafloor sediments have recently been proposed as a potential source of REE. Marine Fe-Mn oxy-hydroxide crusts form by precipitation of dissolved components from seawater. Estimates suggest that an area of just 1 sq. km, surrounding one of the sampling sites in the Pacific, could satisfy one-fifth of the annual world consumption of REE. This emphasizes the importance of marine sediments and other classes of sediments such as seamount Fe–Mn crusts and nodules as possible alternative resources for REE. There is a growing recognition that the cobalt-rich Fe–Mn crusts deposited on the seamounts are potential resources for several strategic metals such as REE and cobalt. The REE-rich mud has high REE contents, 1,000-2,230 mg. kg^{-1} total REE and 200-430 mg. kg^{-1} total HREE. REE contents of the mud are comparable to or greater than those of the southern China ion-absorption-type deposits (ΣREE= 500-2,000 mg. kg^{-1}, ΣHREE= 50-200 mg. kg^{-1}); notably, the HREE are nearly twice as abundant as in the Chinese deposits (Kato et al., 2011).

Depletion of terrestrial mineral resources, has turned our attention to the vast potential of mineral resources within the offshore areas of our country. Geological Survey of India (GSI) has carried out more than 500 cruises within the Exclusive Economic Zone (EEZ) of India and identified heavy mineral deposits within the Territorial Waters (TW) of Kerala and Maharashtra and lime mud along the outer continental shelf and continental slope off Gujarat and Maharashtra (Dinesh, 2014). Now the word is increasingly looking towards offshore regions to meet their mineral and energy requirements. India considering its vast stretch of EEZ has a bright future in offshore mineral explorations. EEZ of India contains massive seafloor sulphides, gas hydrates, manganese micro and macro nodules andphosphates apart from heavy minerals, lime mud and sand. Possibility of identifying REE deposits in EEZ of India is also high considering the favourable tectonic setting of the area.

1.5 Uses of Rare Earth Elements

Although the geochemical properties of REEs are similar, their metallurgical, chemical, catalytic, electrical, magnetic, and optical properties vary, and these unique properties and differences have led to their prominence in a variety of emerging technologies. Rare-earth elements, metals, and alloys that contain them are used in common consumer goods such as computer memory, DVDs, rechargeable batteries, cell phones, vehicle catalytic converters, magnets, fluorescent lighting, and much more. The demand for REEs used in these goods has surged over the past two decades. Many rechargeable batteries are made with rare-earth compounds. Rechargeable lanthanum–nickel–hydride (La–Ni–H) batteries are gradually replacing nickel–cadmium (Ni–Cd) batteries in computer and communications applications and could eventually replace lead–acid batteries in automobiles (Haxel et al., 2002). Although more expensive, La–Ni–H batteries offer greater energy density, better charge–discharge characteristics, and fewer environmental problems upon disposal or recycling. Demand for small, long-lasting batteries is being driven by demand for portable electronic devices such as cell phones, readers, computers, and cameras. Rare earths are used as catalysts, phosphors, and polishing compounds. These are used for air pollution control, illuminated screens on electronic devices, and optical-quality glass. Demand for all such products is expected to rise. Rare-earth elements play an essential role in modern national defence. Night-vision goggles, precision-guided weapons, and other defence technology rely on various rare-earth metals. Rare-earth metals are key ingredients for radar systems, avionics, and satellites.

1.6 Current World Status of REE

Only a few countries produce significant amounts of rare-earth elements. India, Brazil and South Africa were the main producers of REE minerals till 1950s which was taken over by the Mountain Pass rare earth mine in California till late 1980. China is currently the dominant producer of rare-earth elements and more than 95% of the world's REE are produced from two ore deposit types in China ((Haxel, 2005, Humphries, 2010 and Long et al., 2010). The Bayan Obo deposit in China, the largest REE deposit, is a high-grade, igneous related carbonatite deposit that sources 80% of the world's LREE (U.S. Geological Survey, 2011; Kynicky et al., 2012; Verplanck et al., 2014), but this deposit is low in HREE. Out of 95.27 million tons of the world’s rare earth elements resources; China has more than 47 million tons of rare earth oxides.

The ion adsorption clay-type deposits of South China, although small and low grade, dominate the HREE market because they are proportionally HREE enriched and are mined and processed at very low cost (Long et al., 2010; Kynicky et al., 2012). Other countries with notable production in 2009 were: Brazil, India, Kyrgyzstan, and Malaysia; minor production may have occurred in Indonesia, Commonwealth of Independent States, Nigeria, North Korea, and Vietnam (USGS, 2011). Meeting the growing need for HREEs seems daunting because efforts to identify additional economically feasible HREE-enriched deposits have generally been unsuccessful (Long et al., 2010; British Geological Survey, 2011).

Recent exploration all over the world has identified a number of HREE enriched deposits of various types. But the exploitation of REE from many of the deposits isa challenging proposition because REEs reside within a diverse array of fine-grained, refractory minerals that are difficult to physically concentrate and dissolve. Moreover, high Th and U concentrations in these deposits pose environmental concerns (Long et al., 2010). Recently, deep-sea muds have also been proposed as REE resources (Kato et al., 2011), though their profitable exploitation depends on overcoming the technical and environmental obstacles associated with seafloor mining 3–5 km below the surface (Kato et al., 2011). REE in the offshore areas occur either in Fe-Mn crust, pelagic red mud or Fe-Mn nodules. The extraction of REE from all these host sediments is trouble-free as they are devoid of radioactive thorium.

Marine Fe-Mn oxy-hydroxide crusts form by precipitation of dissolved components from seawater. Estimates suggest that an area of just 1 sq. km, surrounding one of the sampling sites in the Pacific, could satisfy one-fifth of the current annual world consumption of REE. These figures emphasize the importance of marine sediments and other classes of sediments such as seamount Fe–Mn crusts and nodules as possible alternative resources for REY. There is a growing recognition that the cobalt-rich Fe–Mn crusts deposited on seamounts are potential resources for several strategic metals such as REE and cobalt.

Now, the world is largely dependent on China for REE, since it is the dominant producer of these metals. The recent restriction on export of REE by China and lack of capacity elsewhere has resulted in steep price rise of REE. Considering the increase in the demand for REE and the deficit in the supply-demand chain, it has become a compulsion of various countries to find new deposits of these metals. At this juncture, it is very essential for our country too to investigate in detail, all possible domains where REE deposits can be found.

1.7 Previous works

Piper, D.Z. (1974), Sholkovitz (1989), Toyodaet.al (1990), Murray et al., (1991), Piperet al., (2007) andCensiet al., (2010) used REE as tracers of sources and processes controlling trace element distribution in marine sedimentsdue to their coherent behaviour.REE distribution in sediments is largely controlled byscavenging processes, in particular by Fe–Mn–oxides (Elderfield et al., (1982), Whitfield and Turner (1987), Elderfield, (1988) and Haley et. al (2004)). Liu et al., (1988) suggested redox conditions of the overlying water column responsible for the REE content in sediments. Chaudhuri and Cullers (1979) and Taylor and McLennan (1985) attributed composition of the terrigenous source responsible for the REE content in marine sediments. Olmez et al., (1991) suggestedfluvial, atmospheric and hydrothermal vent exhalations as the major sources of REE to the ocean.Taylor and McLennan, (1985) suggested REE as a reliable tool for determining depositional processes and sediment provenance, precisely because of their conservative behaviour.

Whitefield and Turner (1979) established the correlation between the concentration ratios of elements in the crustal rocks relative to the seawater and the mean oceanic residence time of elements which are a measure of reactivity of elements in the marine environment. Li (1981) observed a relationship between the concentration of elements in pelagic sediments and seawater. Several investigators identified the factors such as source rock composition, grainsize and mineralogy that control REE distribution in surficial sediments (Cullers etal., 1987; Yang et al., 2002; Borrego et al., 2005; Censi et al., 2007; Prego et al., 2009; Jung etal., 2012). Elderfield and Greaves, (1982) and Fleet, (1984) suggested fluvial, atmospheric and hydrothermal ventexhalations as the major sources of REE to the ocean.

Pattan and Banakar (1993) analysed Manganese nodules taken from a siliceous ooze sediment core in the Central Indian Basin for major, trace and rare earth elements. Fe, P and Ti show a strong positive association with REE suggestingtitanium rich ferri-phosphate as a carrier for REE in the nodules according to their study. In the Central Indian Ocean Basin, REE are generally lower in the calcareous and siliceous ooze than the associatedferromanganese nodules. Red clay has higher REE abundance compared to its associated nodule aswell as siliceous and calcareous ooze. The high REE content in red clay could be due to the presence oflarge abundance of micronodules, smectite and fish teeth which have generally higher REE content (Pattan and Parthiban, 2011).

The rare earth contents of sixteen surficial calcareous sediments from the southwestern Carlsberg Ridge in Indian Ocean were studied by Pattan et al., 1995. The total REE content in these sediments vary between 35mg. kg^{-1} and 126 mg. kg^{-1}. The REE was found to be associated with a combined phase of clays and Mn-Fe oxy-hydroxides. Cobalt-rich Fe–Mn crusts occur on almost all seamounts and plateaus of the world oceans. Fe–Mn crusts are formed through layer-by-layer accretion of colloidal precipitates from cold ambient seawater onto exposed seamount rock substrates. Balaram et al., (2012), have reported high concentrations of rare earth elements and yttrium ranging from 1,727 to 2,511 μg/g in the crust samples collected from the Afanasy Niktin Seamount (ANS) in the Eastern Equatorial Indian Ocean. The concentrations of REE in the ANS Fe–Mn crusts were found to be much higher than those of the mid-Pacific seamount and nodules (1,180–1,434 mg. kg^{-1}). Kuhna et al 1998 studied the layered Fe–Mn crusts from the off-axis region of the Central Indian Ridge north of the Rodrigues Triple Junction and found that an adsorption-desorption equilibrium for the strictly trivalent REE and yttrium with the crust and the seawater. Positive Ce anomalies in the partition coefficient patterns reveal preferential uptake of Ce, but to a lesser extent than in normal hydrogenetic crusts.

Down core variation of rare-earth elements in the authigenic Fe-Mn oxides of a sediment core from the Andaman Sea were studied by Alagarsamy et al., 2010. This study shows positive Ce and Eu anomalies. The positive Ce anomalies are ascribed to oxidation of deep sea sediments and the positive Eu anomalies to the past hydrothermal activity or to the effects arising from sea level changes.

The Ce content and LREE/HREE ratios in Fe-Mn crusts more than 2000 m were lower than those less than 2000 m. The change in REE with water depth could be due to adsorptive scavenging by settlingmatters and behaviours of REE in seawater (Yingchun, et al., (2009)). The higher ΣREE content in sediments from deeper depths along west coast of India is possibly related to the monazite bearing placers, which are widespread in the southern Kerala coast (Siby et al, 2013).

The distribution of REE within the west coast EEZ of India between water depths of 30 m and 200 m, determined using 29 surface sediment samples by Siby Varghese, (2004) has shown higher REE abundance for the coastal areas compared to that of offshore, indicating REE input through river run-off and terrigenous sources. His study indicates Ce as the most abundant element among the REE. The inconsistent relation observed between dissolved oxygen and Ce anomaly in some of the transects, may be due to the influence of high terrigenous sedimentation and along shore currents over the coastal regions.

1.8 Objectives of Present study

The global demand for REE is mostly met by supply from China which produces about 95% of the world's REE output. The recent restriction on export of REE by China and lack of large quantity production elsewhere has resulted in steep price rise of REE. Economic concentrations of REE-bearing minerals are generally hosted in or associated with carbonatites, alkaline igneous rocks, placer deposits and residual weathering deposits as stated earlier. Marine environment also hosts rare earth elements. Seafloor sediments- both shallow and deep water-are found to contain REE minerals in considerable proportions necessitating detailed marine exploration. India has a vast EEZ with geological and tectonic settings favourable for REE enrichment. The Territorial Waters of India cover an area of about 1,15,987 sq.km with known heavy mineral concentration off Odisha, Andhra Pradesh, Kerala and Maharashtra. So a detailed study in these sectors within the inner shelf may be helpful in identifying possible REE enriched zones.

Demand for REE is likely to increase between 10 and 20 % each year. This underlines the need to find more of these resources across the globe. World demand for rare earth metals will continue to grow because high tech products and renewable energy technology are much dependent on them.

The study by Siby Varghese (2004) has revealed REE abundance in the surface sediments within the shallow coastal areas compared to offshorealong west coast of India. His study has covered seabedbetween 30 m and 200 m water depth, mostly within the EEZ beyond the Territorial Water limit. A total of 29 surface sediment samples only were used in this study to cover a very large area of the seafloor, which is quite inadequate. Considering the higher content of REE in the near shore areas and the high national priority to identify areas of REE abundance, this study was taken up to understand the distribution of REE within the inner shelf surface sediments along the west coast of India. For this, 42 surface sediment samples were collected between 2.8 m and 59.7 m isobath,from the inner shelfsector.Since the present study is restricted to the west coast inner shelf with better sampling density, enhanced information about the distributionof REE in the surface sediments is expected.

The important objectives of the present research work are;

1. To study the distribution of REE in the surface sediments within the inner shelf along west coast of India.
2. To understand the role of heavy minerals and sediment texture on the distribution of REE in the inner shelf sediments.
3. To identify promising sectors for detailed exploration of REE within the inner shelf.

CHAPTER 2
STUDY AREA, MATERIAL AND METHODS

2.1 Geomorphology of the Seafloor

India has a vast Exclusive Economic Zone (EEZ) including an area of about 2.16 million sq.km and the Territorial Waters (TW) of India covers an area of about 1,15,987 sq.km in parts of the Arabian Sea in the west, Indian Ocean in the south and Bay of Bengal in the East. The west coast of India, extending from Sir Creek in the north to Kanyakumari in the south, is a trailing passive margin that bears the imprint of generally shore-parallel and less common orthogonal structural elements. The western continental margin of India, which is an Atlantic type passive margin (Biswas, 1982, 1987), was formed following the separation and drifting of Indian landmass from the Gondwanaland during the Cretaceous Period due to sea floor spreading activity of Central Indian Ridge. The western continental margin of the Indian Peninsula, in general, is characterised by:

a) Wide continental shelf, trending NW-SE, with a remarkably straight shelf-edge, limited by the 200 m isobath.
b) A narrow continental slope bound between 200 and 2000 m isobaths and
c) The Arabian abyssal plain.

South of Ratnagiri-Goa, up to Kanyakumari, the presence of Lakshadweep Ridge imparts some complexity to the above physiographic configuration. The continental shelf width varies from 345 km off Daman in the north to 120 km off Goa and tapers to 60 km off Kochi in the south. The western continental shelf of India has an area of about 310 000 sq.km, and is divisible into an inner shelf with modern clayey silt and silty clay sediments with high organic matter and low carbonate content, and an outer shelf having relict carbonate sediments, coarse sands with low organic matter and high carbonates covering the sea floor. The mid-shelf is rather uneven topographically, and the outer shelf is commonly interrupted by shore-parallel ridges and reefs with a relief of 2–18 m. (Faruque and Ramachandran, 2014). The western continental shelf is differentiated into several sub-basins by transverse basement arches or fault bounded highs. These are, from north to south: Kutch, Surat, Ratanagiri, Konkan and Kerala basins, separated by the Saurastra Arch, Bombay High Arch, Vengurla Arch and Tellichery Arch respectively.

The Arabian Sea lies in the north-western Indian Ocean and occupies an area of nearly 750,000 km^2 which constitutes about one-tenth of the area of the Indian Ocean. It is bounded to the west by the Arabia Peninsula and Africa, to the north by Iran and Pakistan, and to the east by India and the Chagos-Laccadive Ridge. Towards south, it extends up to the Mascarene Plateau where it is opened to the north-western Indian Ocean. The Arabian seafloor has about 2.4 km thick sediments overlying a 11.0 km thick crust (Naini, 1980; Naini and Talwani,1982).

2.2 Area of study

The inner shelf of the continental shelf of the west coast of India, covering mostly the Territorial Waters falling mostly within water depths of < 50 m has been chosen for detailed study in this research work. This part of the continental shelf has got a very gentle seaward gradient. Even though the width of the continental shelf is found to varying widely along the west coast, the width of the inner shelf is almost uniform all through the west coast. The work involved during the course of study include sample collection from the seafloor, sample processing, grain size analysis, chemical analysis, computation, preparation of contour distribution map and interpretation. Details of the study carried out during the course of research work are given herein.

2.3 Sample collection

A total of 42 surface sediment samples have been used in this study, out of which 34 samples were collected using Van Veen grab sampler during the cruises of R.V. Samudra Shaudhikama of GSI and were stored in the core repository of GSI at Mangalore.

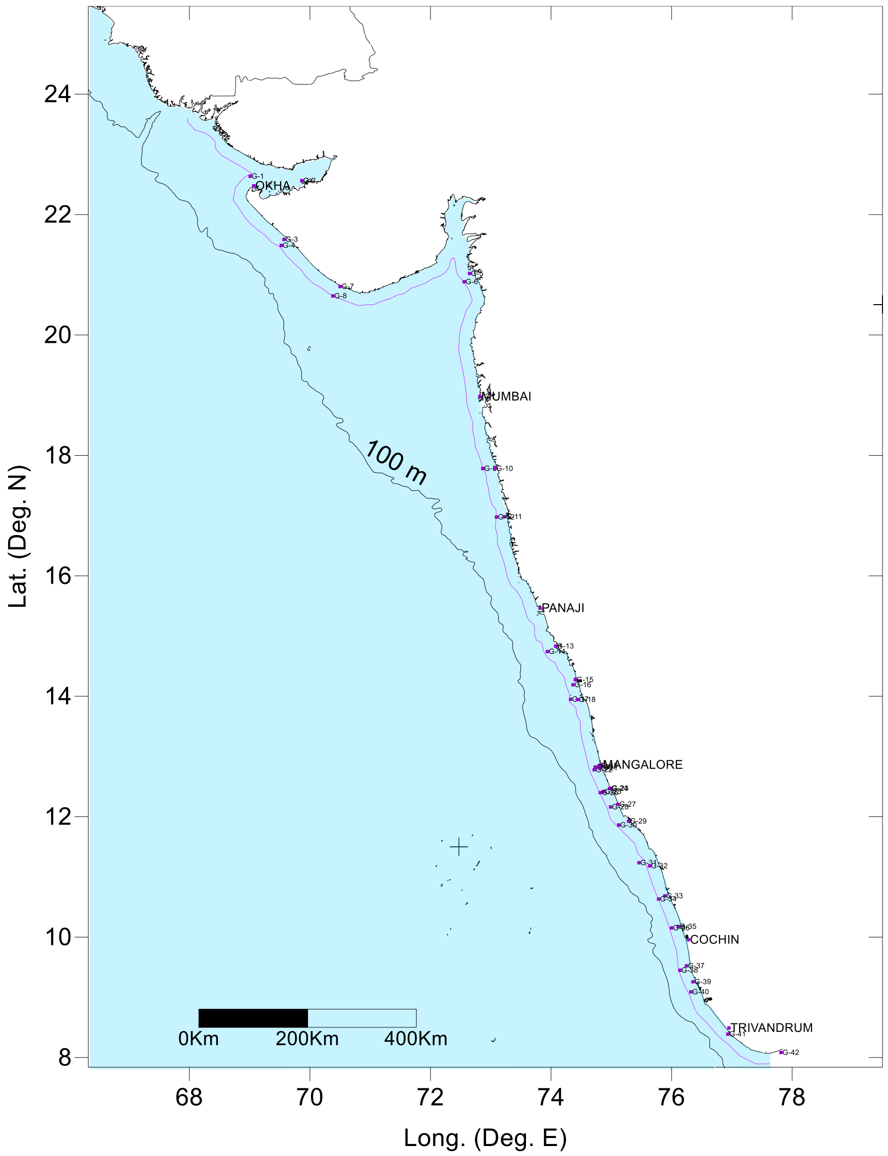


Fig. 2.1 Surface sediment sample locations within the inner shelf.

The remaining 8 surface sediment samples were collected using Van Veen grab sampler at the mouths of four rivers given in the next page.

1. Sharavathi River, Uttara Kannada district, Karnataka.
2. Nethravathi River, Dakshina Kannada district, Karnataka.
3. Chandragiri River, Kasaragod district, Kerala.
4. Karingote River, Kasaragod district, Kerala.

Figure 2.1 shows the locations of the surface sediment samples collected from the inner shelf. The sample locations, sediment type and the REE content of the samples are given in Table 2.1.

2.4 Grain Size Analysis

Study of the grain size and shape of sediments is important in understanding the various mechanisms operative during the formation, transportation and deposition of the sediments. The shape and roundness are important parameters useful in deciphering the nature and transportation of the sediments before being deposited. Wind-transported sediments will be well rounded due to attrition, whereas glacial sediments lack roundness. The sediments transported by running water will show increasing order of roundness depending upon the distance of transportation. Every transporting agent tries to modify the angular, uneven and rough surface of the particles to rounded and smooth (Pettijohn, 1975). Fundamental aspects of grain-size analysis are also detailed by Udden (1914), Wentworth (1922), Krumbein (1934), Krumbein and Pettijohn (1938), Inman (1952), Davis and Ehrlich (1970), Friedman (1979) and Friedman and Sanders (1978).

Sediments are formed by physical/chemical weathering of different rocks present on the earths' crust. Deposition of sediments is largely controlled by various physico-chemical factors of the depositional basin. The size, shape and distribution of particles provide clues to the way in which the material was carried and deposited (Nichols, 2009). Size of a clast depends upon the grain size of the parent rock, distinctiveness of the transporting medium and distance of transport. The size of particles are represented either using phi scale (ϕ) which is the negative logarithm to the base 2 of the particle diameter in millimetres or in metric units.

2.5 Sample Processing

The samples, after drying and homogenisation, were washed repeatedly with deionised water for removing salt. The grain size of the sediments was determined by size analysis following the procedure laid down by Folk, (1966). About 30-35 gm of samples were taken after homogenizing, for sand and 15-20 grams for silt and clay. After adding about 20% H_2O_2 the samples were kept overnight to remove organic matter, if present, washed with de-ionized water two to three times to remove salt, and heating mildly to remove excess H_2O_2. About 10 ml NH_3 was added and magnetic stirring was done for de-flocculation and dispersion and were wet sieved using +230 ASTM mesh. In samples where the coarser fraction exceeds 6% of the total weight of the sample, sieve analysis was carried out at half phi interval using a rotap mechanical sieve shaker and –230 fraction was transferred to the solution prepared for pipetting. Samples in which weight of –230 fraction exceeded 6 % of the initial weight were subjected to pipette analysis (Krumbein and Pettijohn, 1938). The sieve and pipette data were used to prepare cumulative probability curve (Fig. 2.2) for calculating the grain size parameters using graphical method. Various grain size and statistical parameters were computed using the G-Stat software (Dinesh, 2008).

2.6 Cumulative frequency curves

Cumulative frequency curves were drawn by plotting grain sizes on the x-axis and cumulative weight percentages on the y-axis. From the probability chart, the phi values required for the calculation of statistical parameters were determined. The graphic method was used for understanding the grain size distribution. The grain size in phi values was plotted against cumulative weight percentage on a probability chart and different percentile values for 5, 16, 25, 50, 75, 84 and 95(Ø) obtained from the graph were computed for the determination of various grain size parameters. From the cumulative curve, different grain size parameters such as mean, median, mode, standard deviation, skewness and kurtosis were calculated following Folk and Ward, (1957) using G-Stat software programme.

2.7 Statistical parameters in grainsize analysis

2.7.1 Mean

The mean, mode and median collectively referred as the central tendency, help in interpreting the grain size parameters. It is very useful when making inferences using representative samples from a large area.

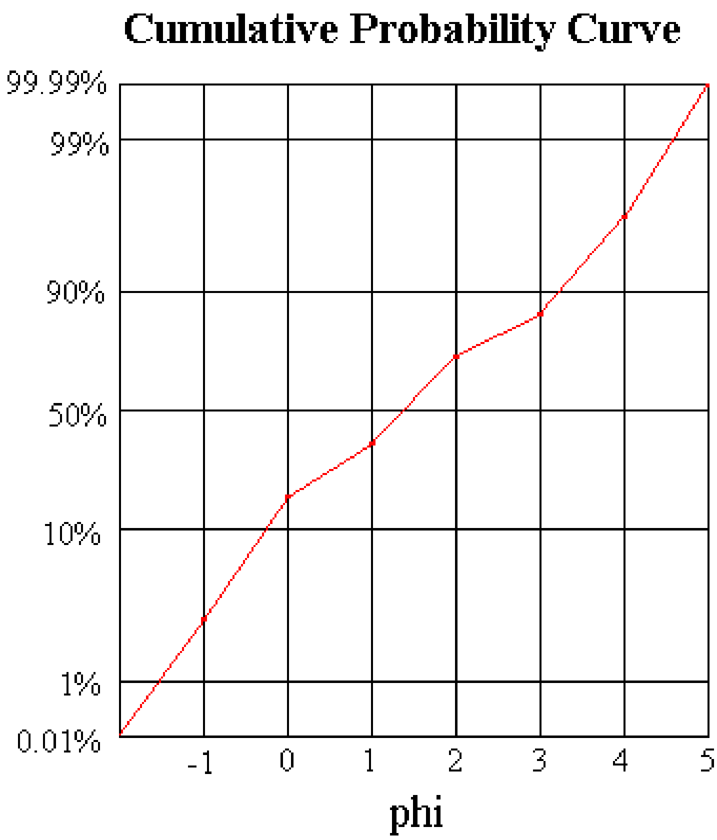


Fig. 2.2 Cumulative probability curve

Mean, median, standard deviation, skewness and kurtosis are used in understanding the grain size variations in relation to environment of deposition and energy conditions of the depositing medium (Folk and Ward, 1957). Mean is calculated using the formula;

$$\text{Mean (Mz)} = \frac{\text{Ø}16 + \text{Ø}50 + \text{Ø}84}{3}$$

The median is the size for which, half of the weight fraction of the sample are coarser and half finer or in other words, it is the value midway in the frequency distribution. It is not sensitive to the exact location of every sample in the distribution, but is used when the mean is very much skewed. Median is not influenced by skewed distributions.

2.7.2 Mode

The value that occurs with the greatest frequency is called mode. Mode is good if the data is quite large in number and also in cases where there are two “typical” data. It ignores most of the information in a distribution and is not suitable if the number of samples is very less.

2.7.3 Standard deviation (SD)

Standard deviation is a measure of the degree of sorting or the uniformity of the particle size distribution. It is a rough measure of the average amount by which observations deviate on either side of the mean. SD also called sorting, is calculated by subtracting the overall mean of the entire data computed from individual mean data. After calculating the square of these differences, they are summed up and divided by the total number of data. The square root of this gives the standard deviation values. Table 2.2 shows ranges of standard deviation.

SD lends itself to computation of other stable measures and is a prerequisite for calculating many of them. SD will be influenced by extreme scores. Fig. 2.3. Fig. 2.4 and Fig. 2.5, the grain sizes in ‘phi’ scale are plotted along x-axis and the wt. percentages of various size fractions along y-axis. The plots show the differences in the nature of curves for well sorted to poorly sorted sediments. Standard deviation is calculated using the formula;

$$\sigma_i = \frac{\text{Ø}84 - \text{Ø}16}{4} + \frac{\text{Ø}95 - \text{Ø}5}{6.6}$$

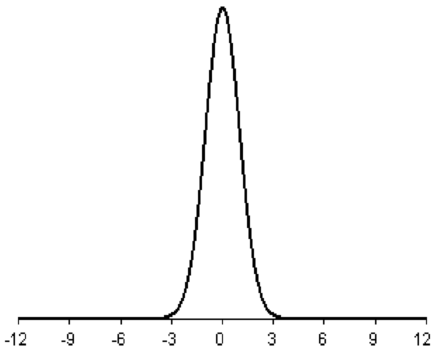


Fig. 2.3Well sorted sediments.

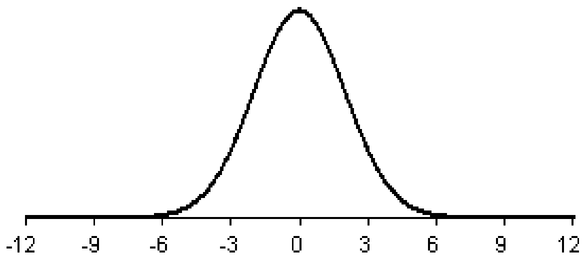


Fig. 2.4 Moderately Sorted Sediments

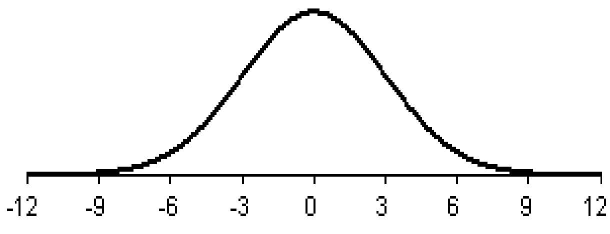


Fig. 2.5 Poorly Sorted Sediments

Table 2.2 Standard deviation or Sorting (σ) Ranges

Very well sorted	<0.35
Well sorted	0.35-0.50
Moderately well sorted	0.50-0.71
Moderately sorted	0.71-1.00
Poorly sorted	1.00-2.00
Very poorly sorted	2.00-4.00
Extremely poorly sorted	>4.00

2.7.4 Skewness (Sk)

Skewness measures the asymmetry of a distribution (Fig. 2.6). If there is more material in the coarser or finer tail of the distribution it is called coarse skewed (negatively skewed) or fine skewed (positively skewed) respectively. Skewness is calculated using the formula given below (Folk and Ward, 1957). Skewness ranges are given in Table 2.3.

$$Sk = \frac{Ø16 + Ø84 - 2Ø50}{2(Ø84 - Ø16)} + \frac{Ø5 + Ø95 - 2Ø50}{2(Ø95 - Ø5)}$$

Table 2.3 Skewness (Sk) Ranges

Very fine skewed	+ 1.0 to + 0.3
Fine skewed	+ 0.3 to + 0.1
Symmetrical	+ 0.1 to - 0.1
Coarse skewed	- 0.1 to - 0.3
Very coarse skewed	- 0.3 to - 1.0

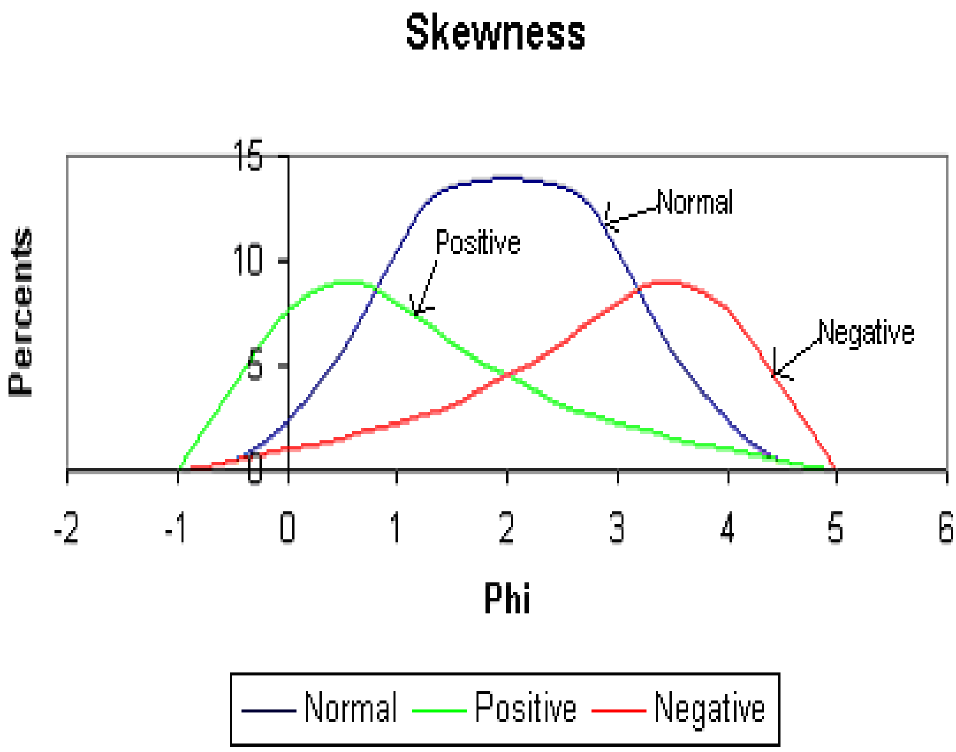


Fig. 2.6 Curves for Normal, Positive and Negative Skewness.

2.7.5 Kurtosis (K_G)

Kurtosis measures the ratio between the sorting in the tails of the distribution and the sorting in the central portion of the distribution (Fig. 2.7). If the central portion is better sorted than the tails, the frequency curve is said to be excessively peaked or leptokurtic. If the tails are better sorted than the central portion, the curve is said to be flat peaked or platykurtic. Strongly platykurtic curves are often bimodal with sub-equal amounts of the two modes. Table 2.4 shows classification based on kurtosis ranges. Kurtosis is calculated using the formula;

$$K_G = \frac{ø95 - ø5}{2.44(ø75 - ø25)}$$

Table 2.4 Kurtosis (K_G) ranges

Very platykurtic	<0.67
Platykurtic	0.67 – 0.90
Mesokurtic	0.90 – 1.1
Leptokurtic	1.1–1.5
Very Leptokurtic	1.5 – 3.0
Extremely leptokurtic	>3.00

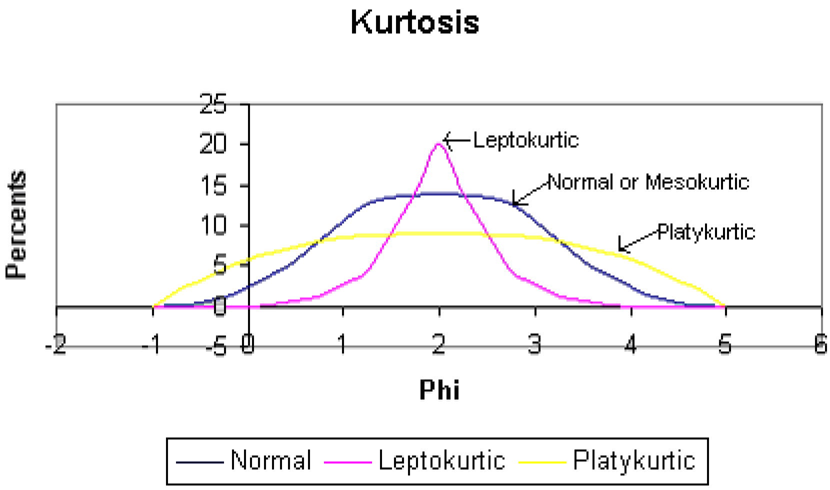


Fig. 2.7 Curves for Normal, Leptokurtic and Platykurtic Sediments.

2.8 Bivariate Plot

A bivariate plot shows the relationship between two variables that have been measured on a single sample. Bivariate plots were used by several workers to understand the relation between the two variables. (Folk and Ward, 1957; Sahu, 1964; Friedman, 1967; and Abed, 1982). The distance to the points from the regression line is called "scatter". A large amount of scatter around the line indicates a weak relationship. Little scatter represents a strong relationship and if all points fall directly on a straight line, a perfect linear relationship exists between the two variables. In the present study, various bivariate plots are used to understand the inter-relation between grain size and statistical parameters.

2.9 Chemical analysis

About 100 gram of the sample was powdered to 270 mesh size using pulverizer, homogenized and then 5 gram of the representative sample was used for chemical analysis. For analysis of the sand, silt and clay fractions, individual fractions were separated from the bulk samples by separating the silt and clay by pipette analysis. The silt and clay fractions were dried at 60°C in the oven and then 5 grams each was submitted for chemical analysis. The samples were analysed for their REE at Regional Chemical Lab of GSI, Hyderabad using Varian-Agilent 7700X ICP-MS and also at Central Geological Lab, CHQ, GSI Kolkata using Perkin Elmer SCIEX ELAN R DRCTM–e ICP-MS technique. The ICP-MS is calibrated by multi-element standard solution to cover the mass range and generate the mass response curve. Matrix matching with a standard reference material (SRM) was used for calibration. International standard GSD-10 and GSD-12 were used for the analysis. Alkali fusion (mixture of lithium metaborate and lithium tetraborate) is used to decompose the fine powdered sediment samples. ICP-MS equipped with a cross flow nebulizer Scott spray chamber was used in the analysis. The ICP-MS, kept in a temperature-controlled laboratory (25 ± 2 °C), was allowed to stabilize before optimization procedures were carried out. The oxide ratio (CeO/Ce^+) and doubly charged ion ratio (Ba^{++}/Ba^+) was found <3 % under full optimum condition.

2.10 Software's used

G-Stat is a software package for grain size statistical analyses and sediment classification. Graphic measures, moment measures, CM diagram, triangular diagrams, cumulative curves, frequency curves, scatter plot etc., can be prepared using this free software de veloped by Dinesh (2008). This software was used in the calculation of grain size statistical analyses, sediment classification, CM diagram and scatter plots used in this study.

Surfer 8.3 version software developed by Golden Software, Inc was used in the preparation of sample location map as well as the surface distribution of various REE within the inner continental shelf along west coast of India as contour map. Surfer is a contouring and surface modelling package that runs under Microsoft Windows. Surfer is used extensively for bathymetric modelling, surface analysis, contour mapping, and 3D surface mapping. A contour map is a two-dimensional representation of a three-dimensional data. The first two dimensions are the X (longitude) and Y (latitude) coordinates, and the third dimension (Z, here REE content) is represented by lines of equal value. The difference between two contour lines is defined as the contour interval. While preparing grid to draw contour lines, a method known as Minimum Curvature was used. Minimum Curvature generates the smoothest possible surface while attempting to honour the data as closely as possible and produces a grid by repeatedly applying an equation over the grid in an attempt to smooth the grid.

MS Excel software by Microsoft was used for data formatting and calculation. Excel is the spreadsheet program essentially having a matrix of rows and columns. Text or numbers can be entered at any position on the work sheet. One can enter a formula in a cell when one wants to perform a calculation and results are displayed.

CHAPTER 3
BATHYMETRY AND SEDIMENTOLOGY

3.1 Introduction:

Indian Ocean is the third largest of the world's oceanic divisions comprising 20% of the total ocean envelope of the earth. It has got an area of 68.556 million sq. km, and is a significant geographic feature of the southern hemisphere. The coast of India starting from the Kori Creek in the northern part of the West Coast extends up to Sunderbans in West Bengal in the east going around Kanyakumari (Cape Comorin) covering a length of approximately 7500 km. The shoreline on the West Coast (mainland) alone is about 3,000 km abutting the Arabian Sea and the Lakshadweep Sea. Nearly half of it falls in the State of Gujarat owing to its sinuous coast line. The rest falls in the States of Maharashtra, Goa, Karnataka, Kerala and Tamil Nadu.

The western coastal plain is relatively narrow with a total absence of deltas. The straight coast line almost parallel to the Western Ghat hill ranges is very striking in the peninsular part. The narrow coastal belt between the Western Ghats and the sea is arranged as step-like terraces in many sections, pointing to the possible effect of recent oscillations in the sea level and submergence. This is evident from the drowned river valleys, lagoons and bars and wave-cut cliffs which are common along the coast line.

The Western Ghats running almost parallel to the West Coast and lying only about 50 km away from the coast is the most prominent physiographic feature of the peninsula. It can be traced over a length of 1,500 km from near the Tapti River in the north up to Kanyakumari (Cape Comorin) in the south. The ranges have a steep and abrupt western front, possibly the result of uplift along an axis parallel to the present-day West Coast. The major rock types, other than

Quaternary alluvial cover near the coastal plains, include the flat lying Deccan basalts in the north, foliated Dharwar Schists and Peninsular Gneisses in the middle and the massive charnockites, khondalites and migmatites in the south.

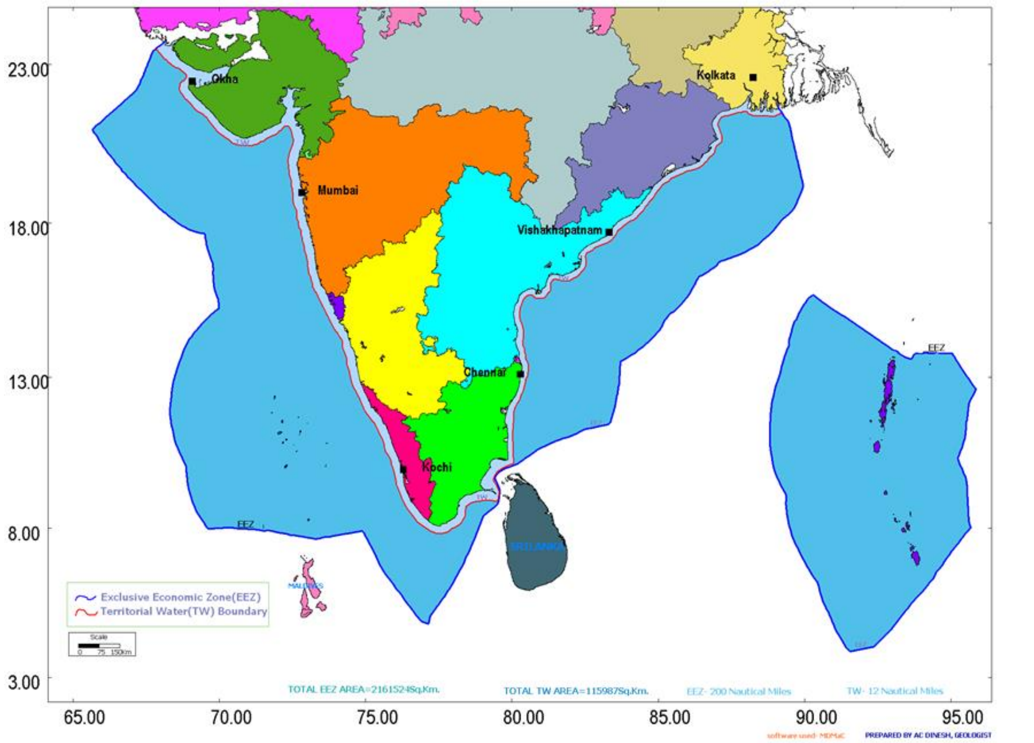


Fig. 3.1 Map showing Exclusive Economic Zone (EEZ) of India,
(After M&CSD, GSI, Mangalore).

3.2 Physiographic Domains

The physiography of the sea floor is highly varied and complicated. The depth to the sea floor varies from less than a meter in the inner shelf to more than 4600 m in the abyssal plain. The continental shelf of the southern West Coast of India is a more or less flat, smooth and generally featureless physiographic unit. In general, the average shelf floor gradient is 1/380. Based on morphology, water depth and distance from the coast the shelf can be separated further in to inner, mid and outer.

3.2.1 **Inner-shelf** The inner-shelf (0-50 m depth) is a more or less flat terrain generally parallel to the coast. The shift in coastline on account of ENE-WSW lineaments has a bearing on the sediment coverage and inner shelf morphology. The bathymetric contours run almost parallel to the coast indicating the absence of any topographical irregularities. Presence of islands and banks mainly off Goa, Karwar, Malpe and Mt.Dilli, locally change the geometry of the inner shelf. Sand bars and beach ridges of the inner shelf often present a wavy pattern in bathymetric contours. Buried palaeo-channels, sunken structures, mounds and rock outcrops are frequently observed in the inner shelf. Isolated biogenic growths are also noticed in this zone indicative of a lowered sea level, where corals thrived under favourable conditions.

3.2.2 **Mid-shelf** The mid-shelf (50-75m) is a monotonous plain, blanketed by recent sediment cover on a pre-existing carbonate platform. The generalized echo character of mid-shelf is distinct echo Type lA (Damath and Dennis, 1997) characterized by sharp and continuous bottom echo with occasional sub-bottom reflectors. This indicates the presence of a thin unconsolidated sediment cover on a pre-existing consolidated sedimentary rock. Interesting topographic features of the mid-shelf include low-resolution topographic undulations and wide sunken structures filled with later sediments. The typical features of the mid-shelf include a series of biogenic reefs running parallel to the coast.

3.2.3 **Outer-shelf** The most prominent part of the continental shelf is the outer-shelf lying between 75 and 300 m water depth. The outer-shelf, in contrast to the inner shelf is mainly composed of carbonate and relict sands. Iron stained quartz and reworked forams are also present. The outer shelf is representative of a sediment-starved Pleistocene plain on which subsequent rapid transgression has denied modern sedimentation. Poorly developed terraces on account of reefal barriers are a common feature of the outer shelf.

3.3 Bathymetry of the Arabian Sea

The bathymetric setup of the Arabian Sea, encompassing the Chagos-Lakshadweep Ridge in particular and its environs, is fairly well known in a generalized way. The pioneering works of GSI and National Institute of Oceanography (NIO) have immensely contributed a wealth of data in this field. Hydrocarbon exploration by Oil and Natural Gas Corporation (ONGC) in the continental shelf and Lakshadweep Trough has necessitated documenting the salient features of the bathymetry (Biswas and Singh, 1988). DSDP drill holes, No. 219. 220 and 221 being in the ridge and adjoining areas, give a fairly good account of the spot depths and subsurface details of the huge stratigraphic column of sediments. Based on gravity and magnetic studies, Naini and Talwani (1982) have divided the morphological setup of the ocean basin into the Western Arabian and Eastern Arabian Basins with Chagos-Laccadive-Laxmi Ridge complex separating the two units. The continental shelf off the West Coast, especially the inner and mid-shelf, has been well-investigated (Nair, 1974, Nair et al., 1978, Nair et al., 1979, Hashimi, 1980). The Marine & Coastal Survey Division of GSI has carried out extensive coastal survey using the coastal vessel R V. Samudra Shaudhikama during 1984-1996.The details of this work is summarized in the unpublished reports of Marine & Coastal Survey Division.

The bathymetric map of Arabian Sea up to 100 m water depth is given in Fig. 3.2. The continental shelf width varies from 345 km off Daman in the north to 120 km off Goa and tapers to 60 km off Kochi in the south. Almost the entire inner shelf falls below <50 m water depth. The gradient of the seafloor is less in the northern parts where the shelf width is more. Minimum shelf width is off Ponnani and from there further south the shelf width is found to be increasing.

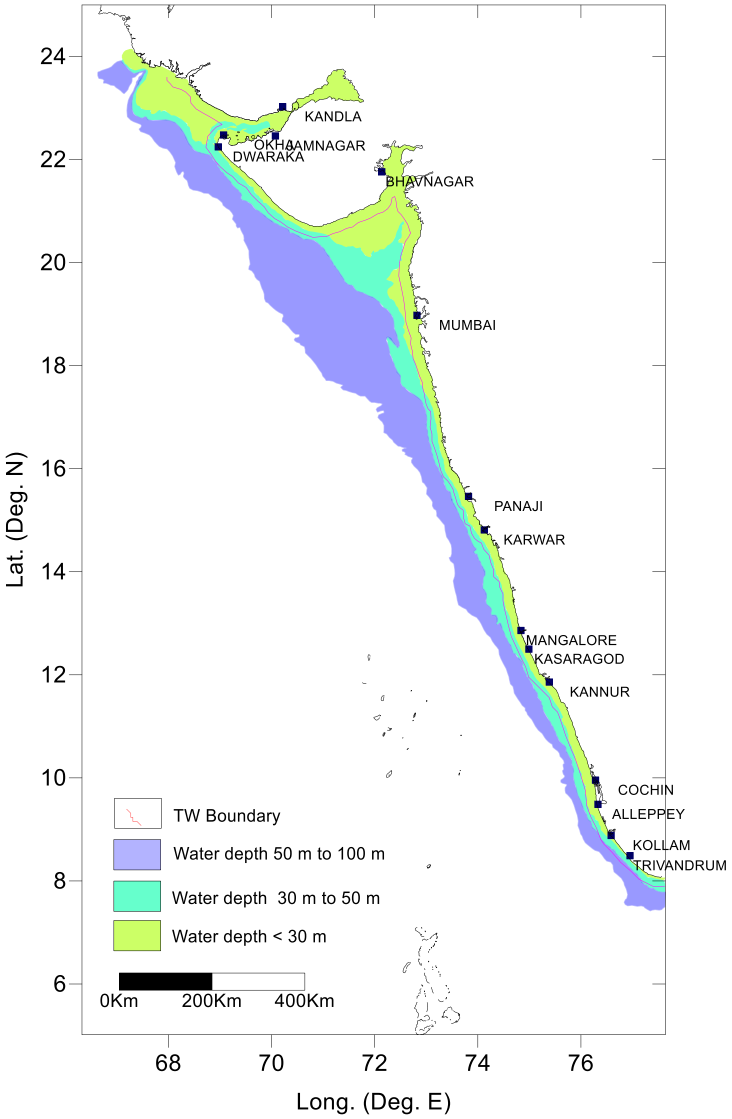


Fig.3.2 The bathymetric map of Arabian Sea, (Modified after M&CSD, GSI, Mangalore).

3.4 Surface sediment distribution

Continental shelf of the West Coast of India receives sediments from geologically interesting hinterland rock formations of different ages. The sediments are drained by fairly dense river systems having high relief-length ratio, transporting millions of tonnes of sediments into the basin. Areal distribution of coastal sediments from Okha to Cape Comorin reflects a complex Quaternary history. Repeated changes in sea level with transgression and regression of sea, accompanied by tectonism and global glaciation had left a strong imprint in the depositional history and also on the bathymetry. The surface sediment distribution map has brought out three distinct broad zones of sedimentation roughly parallel to the coast. The inner shelf is draped with sediments of Pleistocene to Recent Age, with the coarser sediments occupying the beach and the fines in deeper parts of inner shelf.

The inner shelf is covered with sediments of Pleistocene to Recent age. Coarse sediments near to the coast and finer sediments in deep water cover the inner shelf up to 30 m depth. Outer part of inner shelf, middle shelf and outer shelf are covered by sand and gravel units distributed parallel to the coast and are older in age (Pleistocene). Siliceous terrigenous sand occupies middle part of the shelf, described as palaeo-shoreline indicator. In the outer shelf, dead algal carbonate ridges of 2 to 5 m height occur discontinuously as a wall between 85 and 110 m depth. Silty clay is the main sediment type and occurs in all the domains.

The nature and distribution of surface sediments of the west coast was studied earlier by many. The sediments of continental shelf south of Mumbai, Vengurla-Karnataka coast was studied in detail by Nair and Hashimi (1988), Hashimi and Nair (1981). The environmental significance of the western continental shelf sediment was dealt by Gupta (1979). Purnachandra Rao and Wagle (1997) gave a concise account of the shelf morphology and surficial geology of the Western Continental shelf and slope of India. The paper dealt in detail the Late Quaternary Neotectonic activities and subsidence in this area. The surface sediment distribution within the inner continental shelf along the west coast of India is described under three sub-heads for convenience.

3.5 Surface sediment distribution along Gujarat coast

In Gujarat, the Pre-Cambrians are represented by metamorphosed and associated intrusive rocks. Sedimentary rocks of Mesozoic and Cenozoic age and Deccan volcanic of Cretaceous to Eocene age are the other dominant lithologies. The topography of the coastal land is mostly controlled by the geological formations. Tapi, Narmada, Mahi, and Sabarmati draining into Gulf of Cambay are the main drainages in the state.

The western offshore of Gujarat is divided into two major basins viz., Kachchh basin and Saurashtra basin by an almost east west trending Saurashtra arch (Kunduri et al 2006). This arch extends from the land across the shelf plunging into the deep-water realm. The Kutch basin is a pericratonic rift basin at the westernmost periphery of the Indian craton with a southerly tilt (Biswas 2005). Vast stretches of low land plains with a number of creeks, inlets and river mouths are the characteristic feature of the coastal areas adjoining the Gulf of Kutch. Miliolitic limestone exposes almost all through the length of the Saurashtra coast.

The inner shelf area of Gujarat is also covered mostly by silty clay and clayey silt (Fig. 3.3). The seafloor south of Mandovi and north and southeast of Dwarka is rocky and is devoid of sediments. Sand is present within the Gulf of Kutch, southeast of Porbandar and also in the Gulf of Khambhat. The Gulf of Khambhat is the confluence of the major rivers is covered by very fine sand, silt and clay. Fine sediments are strongly fine skewed to coarse skewed near the coast and confluences of rivers suggesting mixing of the relatively coarser material with fine sediments. Seafloor is covered mainly by various sizes of sand in the central part of the area. The areas near to the coast and debouching point of the major rivers are covered by sediments like very fine sand, silt and clay. Sand units ranging in size from very coarse to very fine are dominant in the central part of the basin. Coarser sediments are generally better sorted than the finer silty and clayey sediments. The sediments are strongly fine skewed to coarse skewed to the near coast and mouths of rivers suggesting mixing of the relatively coarser sediments (fine sand and coarse silt) with fines. Heavy minerals present in the area are ilmenite, garnet, rutile, biotite, glaucony, amphibole and epidote in order of abundance (Zaheer et al. 2010). The seafloor in the western part of Mandvi River - Sai Nadi area is covered mostly by greenish brown to olive grey silty clay and clayey silts. The sediment cover is very thin nearer the shore and in the eastern part, due to suspected hard rocky seabed (Rao et al. 2008).

Along Gujarat inner shelf, the coarser sandy sediments in general are better sorted than the finer silty and clayey sediments. The sediments near to the coast and river mouths are strongly fine skewed to coarse skewed suggesting mixing of coarser and finer sediments.

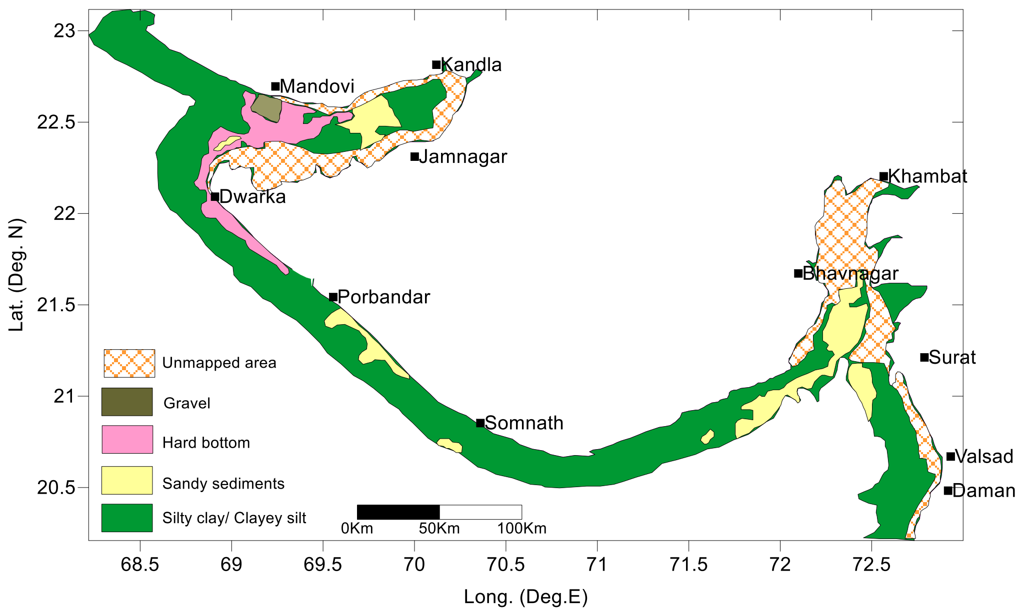


Fig. 3.3 The sediment distribution map within the inner shelf off Gujarat (Modified after GSI, 2016).

3.6 Surface sediment distribution along Maharashtra coast

The Maharashtra coast on a regional scale is quite straight in nature with the hinterlands exposing mostly Deccan trap basalt. Prominent tidal inlets/estuaries are found off Mazgoan, Mumbai, Kalbadevi, Mirya and Mahim. The coast line between Malvan and Vengurla trends almost NNW and SSE direction with exposure of sandy beaches. In some of the coastal belt areas rocky exposures with steep cliffs are also seen. A series of rocky mounds are seen to spread in the sea, away from coast just SSW of Malvan. Thus small bay like formations are seen between coast and the series of mounds. The seabed along this sector slopes in WSW direction in uniform pattern without much undulations. Flattening of the seabed is noticed near the river mouth due to deposition of large quantity of sediments. The gradient of about 1 in 700 indicates a uniformly slopping seabed geometry possibly due to a smoothened seafloor due to the presence of a fine sediment cover. The entire inner shelf of Maharashtra is covered with silty clay and clayey silt reflecting the finegrained nature of the hinterland rocks (basalt). The sediments are mostly olive grey (5 YR 3/2) to greyish brown (5 YR), moderately soft and sticky. Sand was not recovered anywhere in the sampled area. The sediments are poorly to very poorly sorted, negatively skewed, mesokurtic to leptokurtic without HM (Venkatesh et al., 1989). The hinterland comprises flat topped laterite capped hills forming coastal plateaus which abruptly terminate at the coast to give rise to cliffs and escarpments.

The major part of the inner shelf off Maharashtra is carpeted by silty clay and also by clayey silt (Fig. 3.4). Ratnagiri to Alibag, the clay is the dominant sediment with minor pockets of silty clay. Loose, olive coloured clay is the predominant sediment in the seafloor between Umargam and Satpati while the northern part has rocky seabed. The seabed off Satpati to Virar consists of loose brownish clay rich in shells and foraminiferal tests. Silty clay occurs in the area off Virar to Santa Cruz. The sediments are dominantly olive green in colour with very few shells and shell fragments. The sediments collected up to a water depth of 10 m are mostly devoid of shells. Sand size sediment is very poor in this area and occasional increase in coarse material in sediments is mostly due to addition of the skeletal remains (Rao et al. 2002).

The very poorly sorted nature of the sediments along Maharashtra coast indicates prevalence of variable energy condition during deposition. The mean size of sediment in general vary between 6 phi and 10 phi indicating dominance of fine sediments in this sector. This suggest a low energy domain and poor supply of the coarser material. Most of the sediments are fine skewed and platykurtic. The fine skewed nature suggests low energy depositional environment in the area and the platykurtic nature that of poly-modal origin of sediments deposited along this sector. The coarse fraction content is generally very low and the dominant minerals present are quartz, feldspar, pyroxenes and amphiboles (Kumaran et al. 2010).

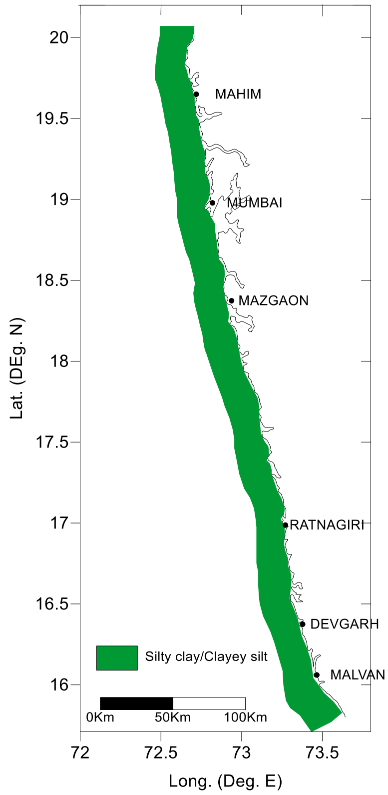


Fig.3.4 The sediment distribution map within the inner shelf off Maharashtra (Modified after GSI, 2016).

3.7 Surface sediment distribution along Karnataka and Goa coast

The maximum shelf width of 120 km is recorded off Karwar and the minimum shelf width of 60 km off Mangalore in this sector. The Western Ghat ranges are present in the east at a distance of 60 km from Karwar, 50 km from Malpe and a maximum distance of 80 km from Mangalore coasts. Ten major rivers are draining the adjoining landmass of this sector. Amongst them the most prominent rivers are Kali Nadi draining near Karwar, Gangawali River and Todri River in Todri, Sharavati River debouching in to the Arabin Sea near Honavar, Sita River in Coondapur, Swarna River in Malpe and Netravati River in

Mangalore. All these rivers flow down the steep Western Ghat slopes and after meandering through the coastal plains join the sea.

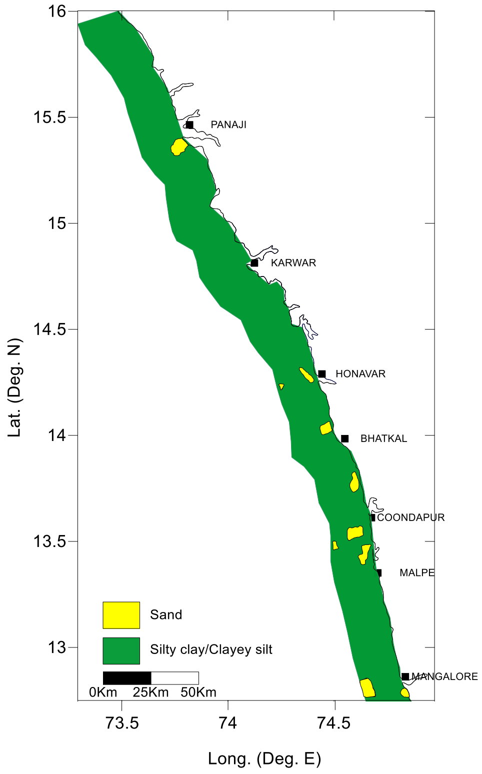


Fig.3.5 The sediment distribution map within the inner shelf off Goa and Karnataka (Modified after GSI, 2016).

There are practically no deltas along the coast and only estuaries are present. The coastal part of Goa and Karnataka is occupied by Gneissic Complex consisting of granites and gneisses of different ages. There are banded migmatites and tonalitic and trondhjemitic plutons with ages ranging from 3400 to 2000 m y. The gneissic terrain is a complex containing several cycles of schist development, granite intrusion and migmatitic transformation (Radhakrishna, 1993., Radhakrishna and Vaidyanadhan, 1994). Isolated patches of Quaternary sediments are exposed all along the coast from Coondapur to Mangalore. Lateritised pebble bed of polymictic nature is exposed at various erosional levels.

The inner shelf off Karnataka and Goa is covered with silty clay and clayey silt except for lenticular bodies of sand present within them (Fig.3.5). It is dark olive gray with shell fragments and carbonaceous matter. Sand bodies are more between Malpe and Honawar and are concentrated close to river mouths. Isolated sand bodies are also present south of Panaji and off Mangalore. Sand is fine to very fine in size and poorly to very poorly sorted. It is mostly made up of detrital quartz of angular to sub angular shape and indicates more than one source of supply. Altered potash and plagioclase feldspars are the abundant constituents after quartz, followed by HM like ilmenite, sillimanite, magnetite and garnet with minor amount of pyroxene. In the shelf part between off-shores of Bhatkal and Coondapur inner shelf sediment are dark olive; intermixed with clay lumps, shells, shell fragments, algal limestone pieces, calcareous concretions, laterite pieces and worm tubes with living organisms. The middle and outer shelves are covered by sediments like silty sand, clayey sand, sandy silt and sand-silt-clay occurring as enclaves within sand rich sediments.

3.8 Surface sediment distribution along Kerala coast

The Kerala coast is mostly straight with a NNW-SSE trend from south of Mangalore to north of Cannanore and thereafter it veers to NW-SE up to north of Calicut and again it changes to NNW-SSE up to Ponnani. The shelf attains the maximum width of 135 km off Mt Dilli and reaches the minimum of 95 km off Ponnani. The Western Ghat occurs about 45 km (average) away from the coast.

Granulites and associated gneisses (Precambrian) are the rock types occurring in the hinterland of this sector. Sporadic Late Precambrian-early Palaeozoic granites and associated pegmatite and Meso-Cenozoic dykes intrude these rocks (Soman, 1997). On-land sedimentary formations are confined to Neogene period and Quaternary period. Both marine and non-marine rocks of the Neogene period fringe the coastal tract between Cannanore and Kasaragod in the north with a maximum width of 10 km at Cheruvathoor. These include rocks comprising gravel, coarse to very coarse sand with grayish clay and carbonaceous clay and seams of lignite. All the rivers in the state originate from the Western Ghat and are short and swift flowing. Periyar River having a length of 244 km is the longest river in Kerala.

Southern part of Kerala, south of Achankovil shear zone, exposes an assemblage of migmatised metasedimentary and metaigneous rocks (khondalite-charnockite assemblages). The largest patch of khondalite group of rocks is noticed south of Achankovil shear in south Kerala. These rock units occur as a linear belt, wedged between charnockite massifs on both sides. Pegmatite phase, closely associated with the younger granite phase is more prominent within the khondalite terrain of south Kerala. In south Kerala, an association of garnet-sillimamte gneiss with graphite, garnet-biotite gneiss and few patches of calc-granulites occur. Tertiary sedimentary formations of Kerala basin unconformably overlie the Precambrian. The name Kerala Basin denotes the southern most part of a great sedimentary province spread over a major part of the western continental margin of the Peninsula (Soman, 1997).

The simplified sediment distribution map within the inner shelf off Kerala is given in Figure 3.6. The shallow part of the seafloor adjoining the coast is mostly covered by silty clay and clayey silt, from north of Quilon to Kasaragod. Sand dominates the shallow seafloor south of Quilon as well as in the deeper part of inner shelf from Vizhinjam to Ponnani. The TW between Ponnani and Kollam is covered with silty clay and clayey silt in the inner part and with sand in the outer part. Sand is the most widespread unit covering the area between outer part of the inner shelf and shelf-edge and represents the palaeo-strand line in this sector.

The sediments are distributed with their longer axis parallel to the coast. Two types of sediments are present in this sector, one occupying the inner part of inner shelf composed of fine sediments between Kasaragod and Ponnani and the second one occupying the inner and inner shelf made up of coarse sediments of terrigenous and biogenetic origin south of Quilon. Outer shelf is covered by fine sediments between Kasaragod and Ponnani and sandy sediments between Ponnani and Quilon. Coarse fraction study indicates that quartz and plagioclase feldspar are the essential constituents of sandy sediments. Magnetite, garnet, zircon, sillimanite, hypersthene, hornblende and clinopyroxene are the minor constituents.

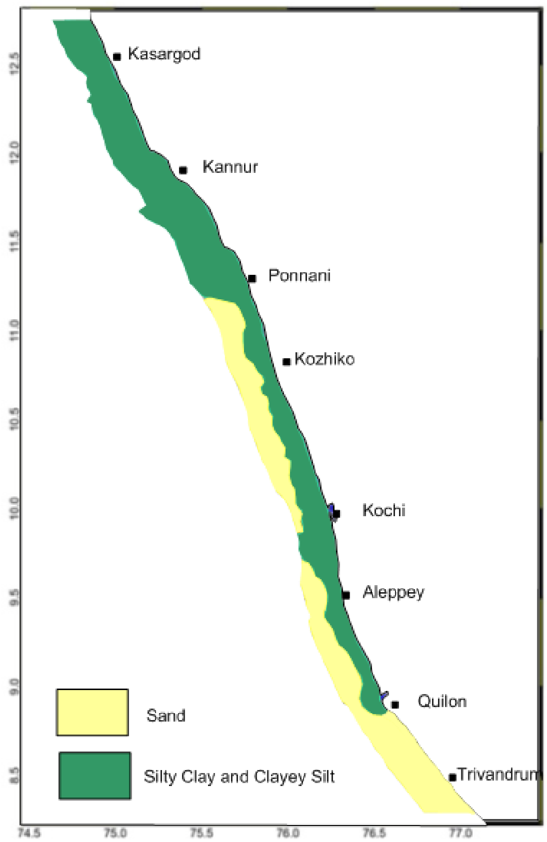


Fig. 3.6 The sediment distribution map within the inner shelf off Kerala (Modified after GSI, 2016).

3.9 Bivariate Plots

The bivariate plots help in understanding the mutual relation between two variables. The grainsize, statistical and other parameters of surface sediments are provided in the Table 3.1. Fig. 3.7 illustrates the relationship between mean size of sediments and standard deviation (SD). Most of the samples plotted are falling in clay category. With a decrease in grain size from 8 phi to 10.5 phi, the SD is showing variation between 2.5 and 3.5 suggesting very poorly sorted nature of the clay sediments. Samples collected off Okha (G-1 & 2), Porbandar (G-4), Karwar, (G-14), Ponnani (G-33), Azhikode (G-36) and Alleppey (G-38) are scattered, possibly suggesting the independent behaviorbetween mean size of sediments and standard deviation (SD). The grain size in general is not showing any appreciable relation with SD which may be due to the extremely finegrained nature of the sediments.

In Fig. 3.8, mean is plotted against skewness. The negatively skewed samples off Azhikode, Pnnani, Alleppey and Okha are scattered below the regression line where as the sample collected off Vizhinjam (G-41) is positively skewed with very high departure from the trend line. Remaining samples are almost clustered within -0.2 and +0.1 suggesting their symmetrical to coarse skewed character. Except two, rest of the samples are of size >8 phi suggesting dominance of clay. The plot suggests change in skewness from positive to negative according to decrease in mean grain size.

Mean is plotted against kurtosis in Fig. 3.9. These two variables are showing marginally small inverse relation. The samples collected off Alleppey (G-37 & 38) and Vizhinjam (G-41) are showing high degree of scattering above the trend line falling in the north-western sector. Samples off Murud (G-9 & 10), Baroda (G-7) are also scattered above the trend line, but in the north-eastern sector. Kurtosis of bulk of the samples is falling within 0.6 and 0.9 indicating their platykurtic nature suggesting polymodal origin. The sediments off Alleppey and Vizhinjam are leptokurtic to very leptokurtic pointing towards a unimodal genesis.

The covariance between skewness and kurtosis is illustrated in Fig. 3.10. Here the trend line is showing slight slope away from the origin suggesting their inverse relationship. Most of the samples are falling between +0.2 and -0.2 and kurtosis values between 0.6 and 0.9, indicating their fine to coarse skewed and platykurtic nature.

Fig. 3.11 depicts the relation between SD and skewness. The SD of the samples range between 1.73 and 3.33 indicating poorly to very poorly sorted nature of the sediments in the inner shelf.

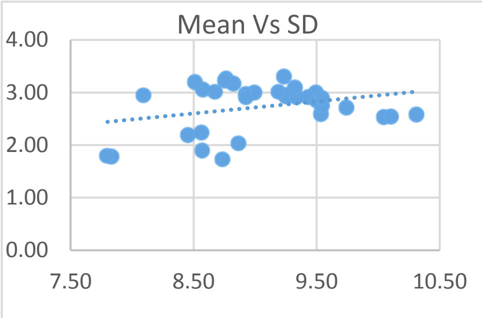


Fig. 3.7 Mean Vs SD

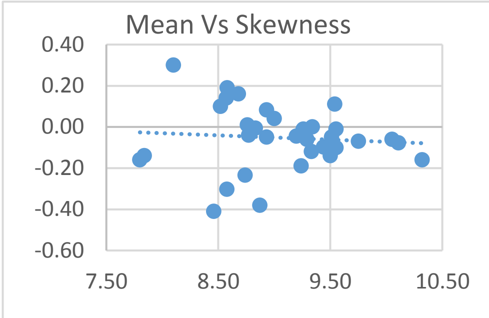


Fig. 3.8 Mean Vs Skewness

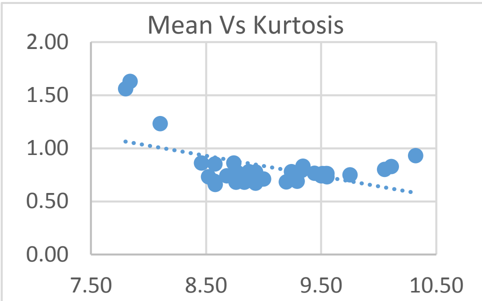


Fig. 3.9 Mean Vs Kurtosis

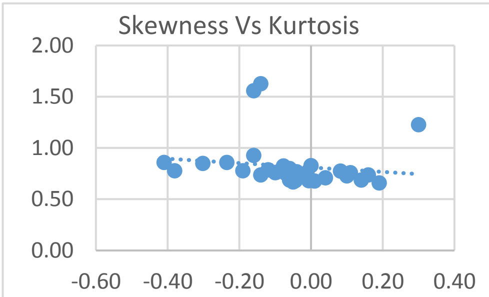
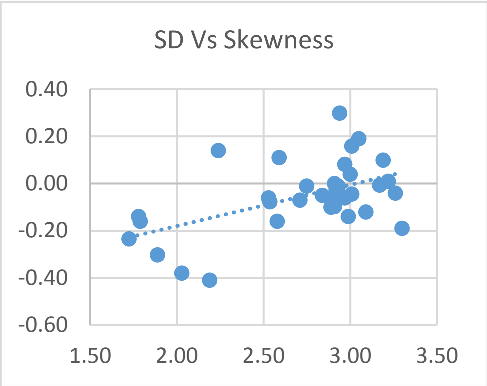


Fig. 3.10 Skewness Vs Kurtosis

The plot shows a visible clustering of most of the samples and an inconspicuous and widely dispersed cluster of six samples which is proximal to the origin of the plot (G-1, 2,33,36,37 and G-38). Out of these six points, G-2 occupies on the trend line itself whereas G-37 and G-36 are located farthest from the trend line showing maximum scattering. Remaining samples are part of the bigger cluster seen in the NE end of the regression line. G-41 collected off Vizhinjam followed by G-4 and G-3 off Porbandar are scattered more towards the north of the trend line where the SD range is high. G-34 off Ponnani shows maximum dispersion from the trend line. The linear regression line is suggesting a sympathetic relation between SD and skewness. Fig. 3.12 shows mutual relation between SD and kurtosis. Most of the sample points are falling in a linear pattern except three samples which show marked deviation. These three samples were collected off Alleppey (G-37 and 38) and one off Vizhinjam (G-41). The clustering is very prominent for samples falling within a range of 2.5 to 3.3 for kurtosis and 0.6 to 0.9 for SD. The linear regression line suggests an inverse relation between SD and kurtosis.



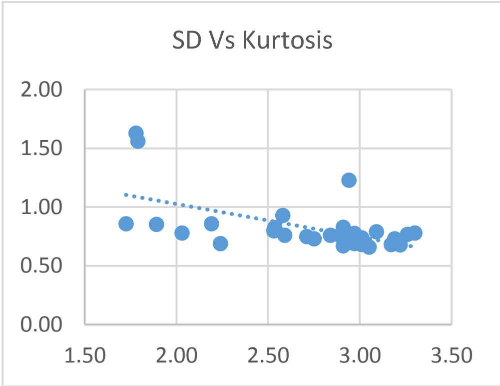
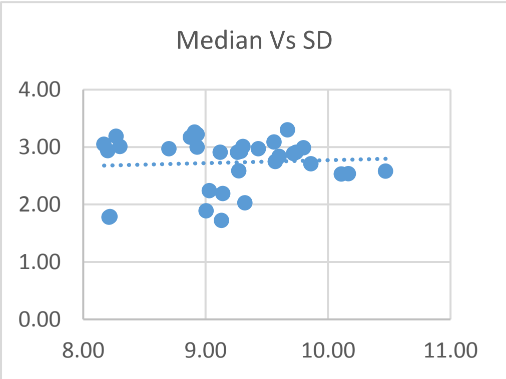


Fig. 3.11 SD Vs Skewness

Fig. 3.12 SD Vs Kurtosis



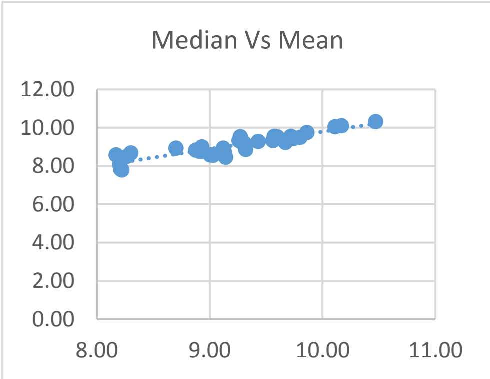


Fig. 3.13 Median Vs SD

Fig. 3.14 Median Vs Mean

Median against SD is plotted in Fig. 3.13. Here six samples (G-1, 2, 4, 33, 36 and 38) are showing deviation from the trend line. SD for these samples are < 2.5 suggesting their relatively better sorted nature compared to the remaining poorly sorted sediments. The trend of the regression line is mildly sloping towards the origin of the plot indicating a direct relation between median and SD. Fig. 3.14 illustrates the relation between median and mean. In a distribution the mean and median will be same, when energy condition is uniform. Such samples when plotted fall on a single point or form a very close cluster. When the grain size of the sediment varies conspicuously, both mean and median are forming separate clusters. In Fig. 3.14, mean and median follow a linear trend with a sympathetic relation.

3.10 Conclusion

The sediment distribution map within the inner shelf along the west coast suggest dominance of sandy sediments south of Kollam, sand and silt and clay sediments sharing the outer and inner shelf between Kollam and Ponnani and dominance of slit and clay north of Ponnani. Along Karnataka, Goa and Maharashtra coast silt and clay cover the seafloor of the inner shelf with pockets of sand. Even though silt and clay are the main sediment type covering the inner shelf along Gujarat coast, larger sand bodies and isolated gravel are also present in this sector. In some places the seafloor is rocky. The sediment distribution is mostly controlled by the seafloor topography. Silty clay and clayey silt are the dominant sediment type of the area. Finer fractions in the size class of silty clay and clayey silt occurs in the deeper parts on either side of the topographic high off the Gulf of Kutch. Sand with various proportions of silt and clay occurs on the topographic highs. This distribution pattern may be the result of instability of the finer grains on the topographic highs due to high energy conditions prevailing in the inner shelf and also duo to the winnowing effect by the currents.

The grain size in general is not showing any appreciable relation with SD which may be due to their extremely finegrained nature. Skewness shows change from positive to negative according to decrease in grain size. Mean and kurtosis show weak inverse relation. Kurtosis for majority of the samples is falling within 0.6 and 0.9 suggesting polymodal origin. Most of the samples are fine to coarse skewed and platykurtic. SD and skewness, and SD and median show sympathetic relation. Skewness and kurtosis, SD and kurtosis, and median and mean show inverse relation.

CHAPTER 4

DISTRIBUTION OF REE IN THE SEAFLOOR SEDIMENTS

4.1 Distribution of REE in Surface Sediments off Gujarat and Maharashtra Coast

REE in the inner shelf sediments off the Gujarat and Maharashtra coasts vary between 106.53 mg. kg^{-1} and 154.48 mg. kg^{-1} and their distribution is depicted in Fig. 4.1 as contour map. The average REE content in sediments is 126.49 mg. kg^{-1} with a SD of 12.97. The sediments all along Gujarat and Maharashtra offshore show moderately high REE except in Gulf of Khambhat and Gulf of Kutch. Along the coastal stretch of these two states, REE content is moderately high in the surface sediments between Dwarka and Jakhau, Malvan and Devgarh, Mahim and Daman. The low REE in the nearshore sediments in Gulf of Khambhat and Gulf of Kutch could be the resultant of intense dilution by the sediment flux from the rivers debouching into the Gulfs as well as low REE signature of the source rocks. REE in general show increase with decrease in sediment size and increase in heavy mineral fractions (Singh, P and Rajamani, V, 2001).

4.2 Distribution of LREE in Surface Sediments off Gujarat and Maharashtra Coast

Incidence of LREE in surface sediments along Gujarat and Maharashtra coast is low and its content ranges between 89.34 mg. kg^{-1} and 137.72 mg. kg^{-1} with an average of 109.04 mg. kg^{-1} and SD of 12.66. The low SD value suggests presence of relatively uniform LREE in sediments. The maximum content is recorded in the area off Jakhau and south of Devgarh, whereas, the inner parts of Gulf of Khambhat and Gulf of Kutch contains the lowest concentration of LREE (Fig. 4.2). A relative drop in LREE compared to the rest of the sectors is observed between Mazgoan and Ratnagiri and also off Surat and Alang sector.

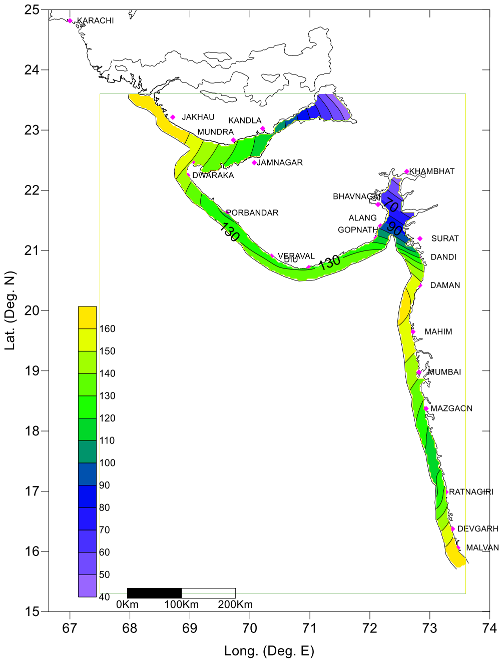


Fig. 4.1 Contour Map showing distribution of REE in the surface sediments within the inner shelf off Gujarat and Maharashtra.

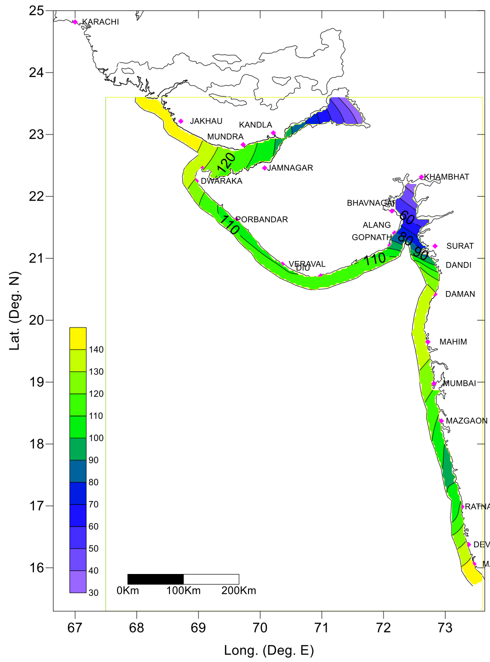


Fig. 4.2 Contour Map showing distribution of LREE in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Incidence of Lanthanum in the surface sediments off Gujarat and Maharashtra ranges from its lowest value of 5 mg. kg^{-1}to highest concentration of 40 mg. kg^{-1} (Fig. 4.3). There are only three sectors where the LREE content is relatively higher being 30 mg. kg^{-1} to 40 mg. kg^{-1}. These are Jakhau-Mundra in the extreme north of Gujarat, Daman-Mumbai sector of Maharashtra north sector and the southern-most being Devgarh-Malvan sector. In the Gulf of Khambhat and Kutch the incidence of Lanthanum is lowest at 10 mg. kg^{-1}. The low incidence could be due to sediment input from the rivers diluting the concentration level of Lanthanum in these two sectors. Narmada, Tapti and Sabarmati rivers dump sediments in the Gulf of Khambhat and cause dilution in its concentration.

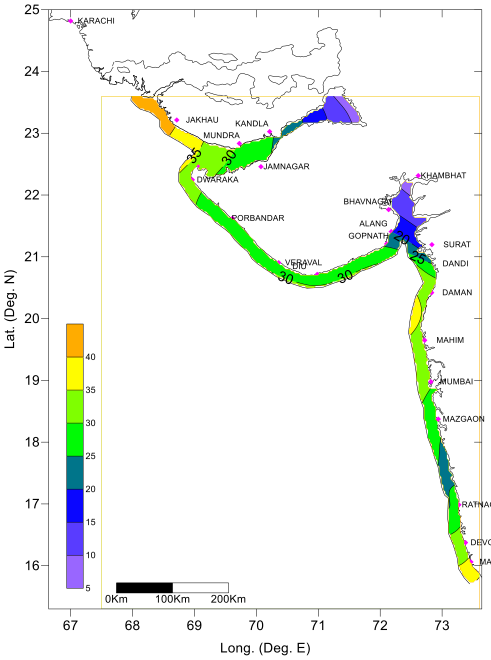


Fig. 4.3 Contour Map showing distribution of Lanthanum in the surface sediments within the inner shelf off Gujarat and Maharashtra.

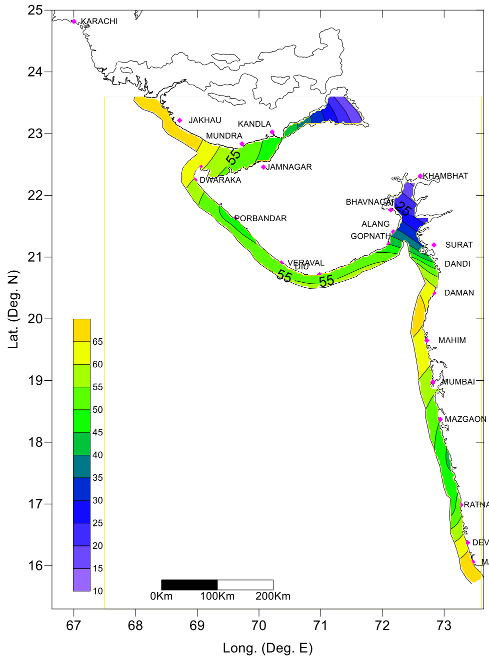


Fig. 4.4 Contour Map showing distribution of Cerium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Except that the concentration of Cerium in the inner shelf sediment is slightly higher than that of La, the pattern of distribution of both these metals is similar (Fig. 4.4). Ce concentration is higher in three sectors: 1. Mundra-Jakhau sector, 2. Daman-Mumbai sector, in the north Maharashtra and 3. Devgarh-Malvan sector with Ce concentration level varying from 55 mg. kg^{-1} to 65 mg. kg^{-1}. Entire Kutch peninsula from Porbandar to Gopnath has a moderate 50-55 mg. kg^{-1}. The shelf off Mumbai to Ratnagiri is also having a moderate Cerium content in the inner shelf sediment. Except in the Gulf of Khambhat where the drop from 60 mg. kg^{-1} to 20 mg. kg^{-1} is rapid in a short distance along the shelf down south.

Incidence of Praseodymium in the inner shelf sediments is rather low and varies from 2 mg. kg^{-1} to 8 mg. kg^{-1} (Fig. 4.5). Identical to the distribution of LREE, Pr also shows higher concentration in three sectors. The distribution pattern of Praseodymium is similar to La and Ce where these elements display lower level of incidence in the Gulf of Kutch and Gulf of Khambhat. The shelf sediments in these three sectors contain 7 mg. kg^{-1} to 8 mg. kg^{-1} of Pr. River inputs in the Gulf of Kutch and Khambhat result in lowering the concentration of Pr in the surface sediments due to dilution.

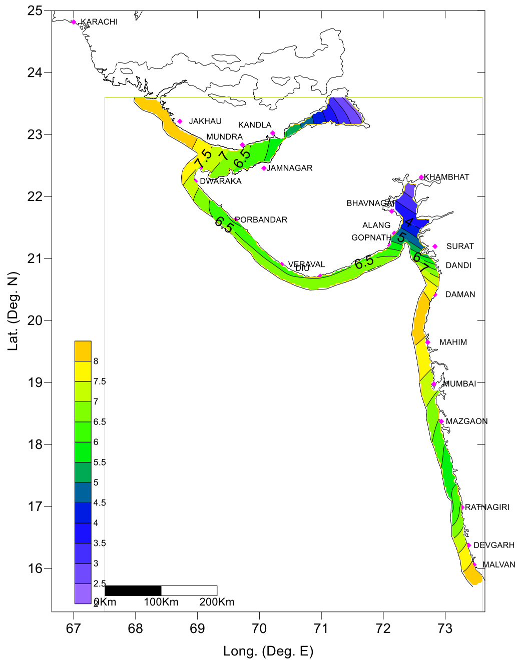


Fig. 4.5 Contour Map showing distribution of Praseodymium in the surface sediments within the inneshelf off Gujarat and Maharastra

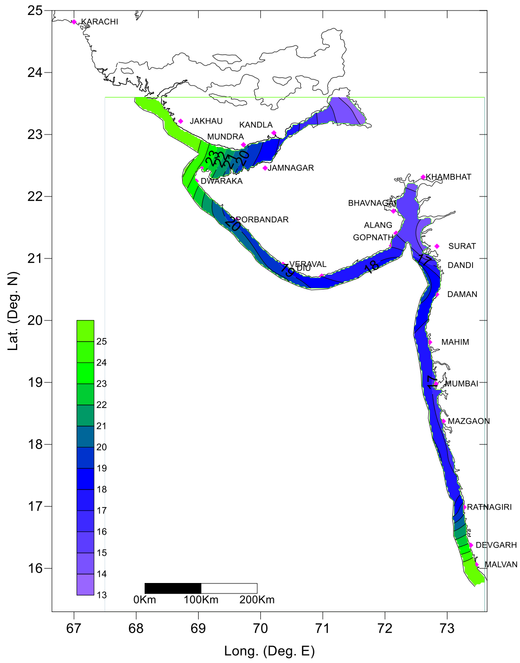


Fig. 4.6 Contour Map showing distribution of Neodymium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Distribution of Neodymium in the inner shelf sediments off Gujarat and Maharashtra coast is a little different from that of LREE distribution in these shelves. A long stretch of the shelf from Porbandar in Gujrat to Ratnagiri in Maharashtra the higher concentration is seen only in two sectors unlike that of Lanthanum and Cerium (Fig. 4.6). Jakhau-Dwarka sector and Devgarh-Malvan sectors show relatively higher concentration of 22 mg. kg^{-1} to 25 mg. kg^{-1} of Neodymium. From Porbandar to Ratnagiri the incidence of Nd in the sediment is 14 mg. kg^{-1} to 20 mg. kg^{-1}. Dilution is due to sediment input from the corresponding rivers.

Incidence of Samarium is very low in the surface sediments of inner shelf off Gujrat and Maharashtra coast, ranging from 3.6 mg. kg^{-1} to 5.2 mg. kg^{-1} (Fig. 4.7). Higher concentration is seen in three sectors 1. Jakhau-Dwarka in the NW extreme of Gujrat, 2.Dandi-Mahim sector and 3.Ratnagiri-Malvan in the southern sector off Maharashtra coast.

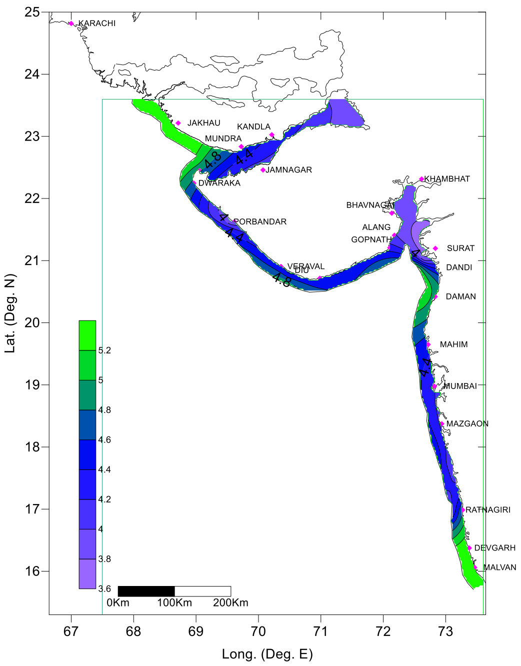


Fig. 4.7 Contour Map showing distribution of Samarium in the surfacesediments within the inner shelf off Gujarat and Maharashtra.

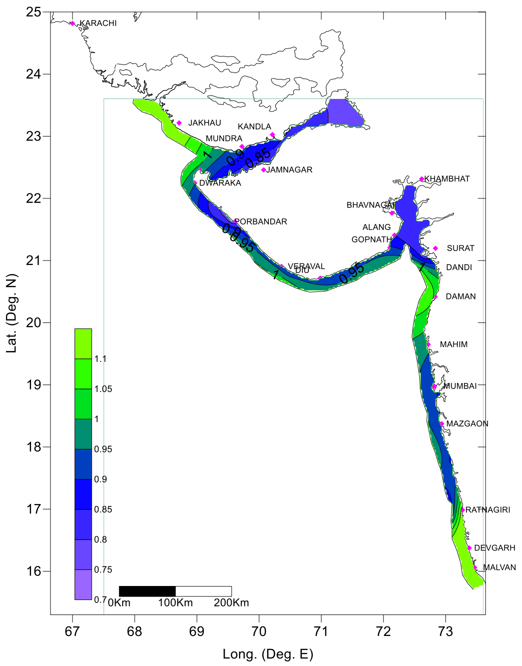


Fig. 4.8 Contour Map showing distribution of Europium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

The shelf sediments off Dwarka to Gopnath and off Mumbai to Ratnagiri contain 4.2 mg. $kg^{-1}$to 4.6 mg. kg^{-1} of Sm. Gulf of Khambhat and Kutch carry lowest incidence of Sm 3.6 mg. kg^{-1} to 4.2 mg. kg^{-1} due to dilution by the sediment influx from the rivers debouching in the gulfs. Absence of major drainage in the Jakhau-Mundra and Devgarh-Malvan sectors helped in the development of higher concentration levels of Sm in these sectors.

Europium content is very low in the surface sediments of inner shelf along the coast of Gujarat and Maharashtra, ranging from 0.7 mg. kg^{-1} to 1.10 mg.

kg^{-1}. There are three sectors in the Gujarat-Maharashtra inner shelf which show relatively higher concentration 0.1 mg. kg^{-1}to 1.1 mg. kg^{-1}of Europium: 1. Jakhau-Dwarka in the northwestern part of Gujrat, 2. Dandi-Mahim sector of south Gujarat and north Maharashtra and 3. Ratnagiri-Malvan in the southern extreme of Maharashtra shelf (Fig.4.8). Medium range of concentration of Eu from 0.85 mg. kg^{-1} to 0.95 mg. kg^{-1} occurs in two sectors of longer stretches: 1. Dwarka-Gopnath in the Kutch peninsula and 2. Mahim-Ratnagiri shelf off Maharashtra coast. Lowest concentration of 0.7 mg. kg^{-1} to 0.85 mg. kg^{-1} of Eu in the inner shelf sediments was recorded in the Gulf of Kutch and Gulf of Khambhat. River-borne sediments reaching the shelf have caused the dilution of Eu in the shelf sediments of the Gulfs.

4.3 Distribution of HREE in Surface Sediments off Gujarat and Maharashtra Coast

The HREE content in the inner shelf sediments vary between 14.95 mg. kg^{-1} and 20.43 mg. kg^{-1} with an average of 17.46 mg. kg^{-1} and SD of 1.65. The HREE content in sediments along this segment is very low compared to that of southern Kerala. The higher content is found between Surat and Malwan along the southern sector whereas moderate content is recorded along the Saurashtra and Kutch coast (Fig. 4.9). The mean as well as low standard deviation point to relatively uniform content of HREE in the shelf sediments. The low content recorded both in the Gulf of Khambhat and Gulf of Kutch possibly indicates dilution by fluviatile sediments.

Gadolinium content is low in the surface sediments of inner shelf along the coast of Gujarat and Maharashtra, ranging from 4.5 mg. kg^{-1} to 6.05 mg. kg^{-1} with a mean of 5.2 mg. kg^{-1}. The SD of 0.48 for Gd indicate uniform content of this metal in the surface sediments. Gd content is more in sediments between Surat and Ratnagiri and off Jakhau (Fig. 4.10). Moderate content is observed in rest of the shelf sediments.

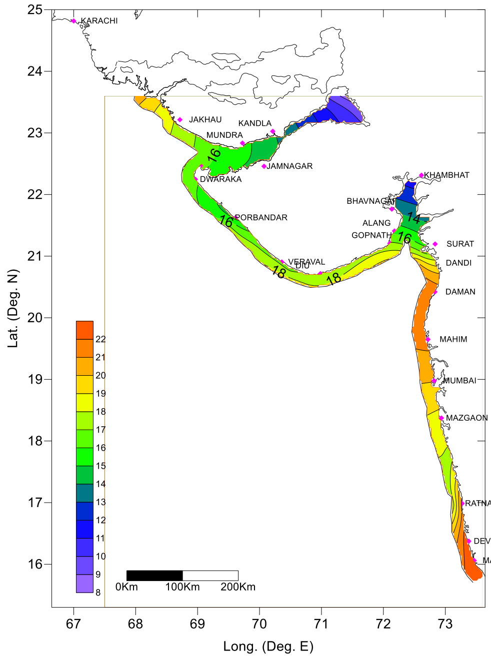


Fig.4.9 Contour Map showing distribution of HREE in the surface sediments within the inner shelf off Gujarat and Maharashtra.

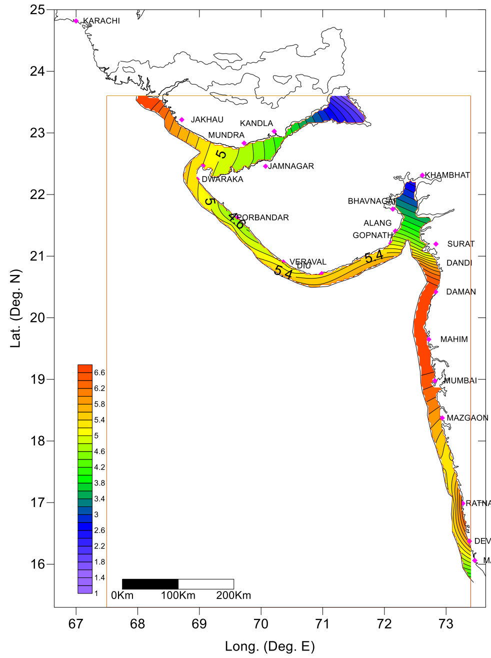


Fig. 4.10 Contour Map showing distribution of Gadolinium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Terbium content is very low in the surface sediments of inner shelf ranging from 0.69 mg. kg^{-1} to 0.94 mg. kg^{-1} with a mean of 0.80 mg. kg^{-1}. The SD of 0.08 for Tb indicate uniform content of this metal in the surface sediments. Tb content is more in sediments between Dandi and Mumbai, south of Ratnagiri and off Jakhau (Fig. 4.11). Moderate to low content is observed in rest of the shelf sediments.

The distribution of dysprosium is shown in Fig. 4.12. Its content ranges from 3.82 mg. $kg^{-1}$to 5.76 mg. kg^{-1}. The mean content in sediment is 4.71 mg. kg^{-1} and the SD is 0.57. The sediments south of Surat up to Malwan contain relatively higher Dy than that of Saurashtra and Kutch coast. The content of Dy is very low in the entire inner shelf which is dominated by silty clay and clayey silt. The low SD is pointing to the uniform content of Dy in the surface sediments.

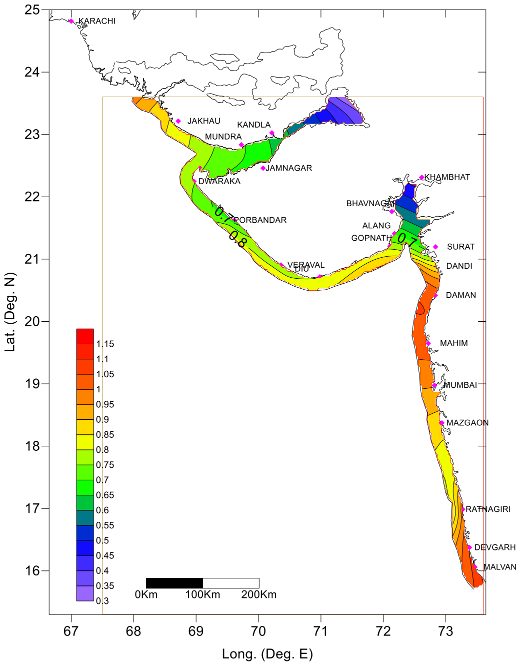


Fig. 4.11 Contour Map showing distribution of Terbium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

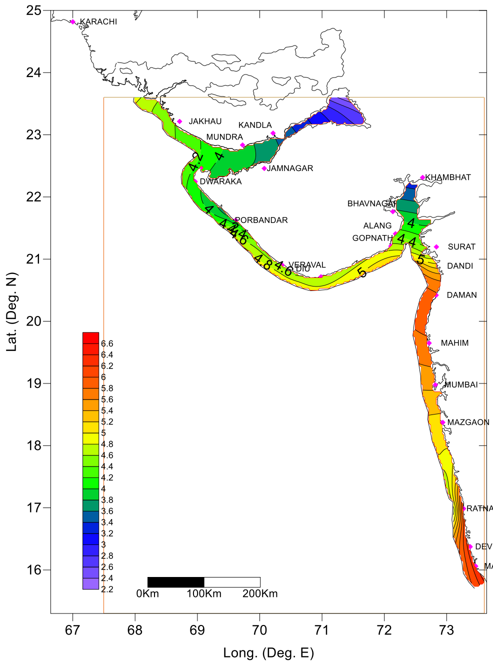


Fig. 4.12 Contour Map showing distribution of Dysprosium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Like other HREE, holmium content is also insignificantly low in the sediments as illustrated in Fig. 4.13. Its content varies from 0.72 mg. kg^{-1} to 1.06 mg. kg^{-1} with a mean of 0.88 mg. kg^{-1} and SD of 0.10. Its distribution pattern is almost identical with that of Dy. Relatively higher content is found in the inner shelf between Surat and Malwan. Ho is found to be low off Saurashtra and Kutch coast.

The distribution of erbium is shown in Fig. 4.14. Its content ranges from 2.07 mg. kg^{-1} to 2.89 mg. kg^{-1}. The mean content in sediment is 2.47 mg. kg^{-1} and the SD is 0.25. The shelf sediments between Surat and Malwan contain relatively higher Er than that off Saurashtra and Kutch coast. The Er content shows minor variation from the mean value which is also reflected by the standard deviation suggesting its uniform content in sediments.

Thulium content in sediments varies between 0.47 mg. kg^{-1} and 0.50 mg. kg^{-1} with an average of 0.49 mg. kg^{-1} and a SD of 0.01. This suggests its insignificant content in the entire sector. The content is extremely low in the Gulf of Kutch, Gulf of Khambhat and south of Ratnagiri (Fig. 4.15).

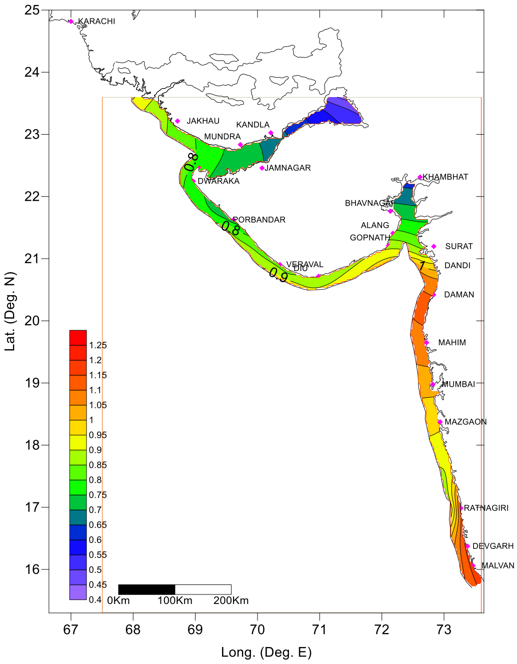


Fig. 4.13 Contour Map showing distribution of Holmium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

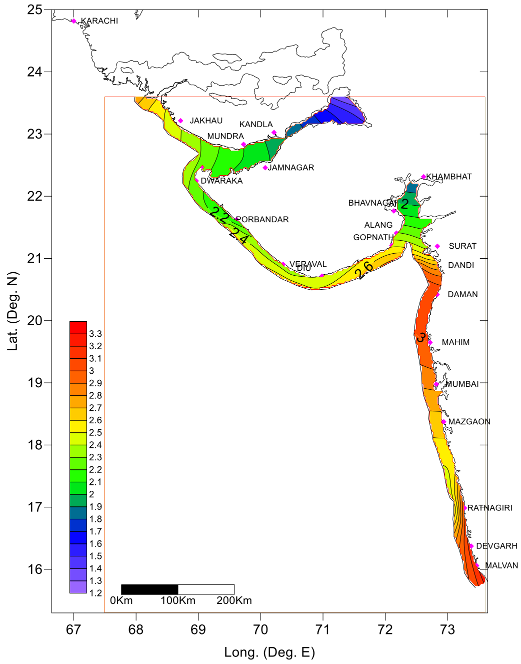


Fig. 4.14 Contour Map showing distribution of Erbium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Distribution of Ytterbium is shown in Fig. 4.16. Its content shows variation between 2.05 mg. kg^{-1} and 2.73 mg. kg^{-1}. Its presence in sediments is very negligible and the mean value suggest the availability of this element in nearly uniform manner in sediments. The contour distribution map also illustrates its uniform content along the Maharashtra and Gujarat coast except in the Gulf of Kutch, Gulf of Khambhat.

Lutetium like other HREE also show extremely low content in the shelf sediments with its content showing variation from 0.47 mg. kg^{-1} and 0.50 mg. kg^{-1} with an average of 0.49 mg. kg^{-1} and a SD of 0.01. The low SD is indicative of near uniform content of Lu in the shelf sediments. Saurashtra as well as sector between Surat and Ratnagiri contain relatively more Lu compared to rest of the inner shelf (Fig. 4.17).

4.4 Distribution of REE in Surface Sediments off Goa and Karnataka coast

The inner shelf is covered mostly by silty clay and clayey silt with small sand bodies off Goa and Karnataka. REE in sediments vary between 36.44 mg. $kg^{-1}$and 174.6 mg. kg^{-1}. ΣREE of samples collected from Mandovi estuary showed significant correlation with clay and silt fractions and its content in sediments is primarily controlled by its texture and REE signature of source sediment (Prajith et al. 2015). Shynu et al. (2013) suggested consistent REE patterns of sediments from Zuari estuary and adjacent continental shelf which may be reflecting the composition of the dominant detrital minerals delivered to the estuary/shelf. The distribution shows a central low between Karwar and Bhatkal with moderate high sectors lying north and south of it. Compared to Kerala offshore, the REE content is low along the Karnataka inner shelf (Fig. 4.18).

The REE is consistently high in the inner shelf of Goa-Karwar. The REE is low between Bhatkal and Karwar with moderately high level of incidence (>115mg. kg^{-1}) located in the inner shelf between Bhatkal and Mangalore which further south merges with the low REE sector off Kasaragod along northern Kerala. The low incidence of REE in the central part between Karwar and Bhatkal can be attributed to dilution due to sediment influx from the river Sharavathi. The low concentration sectors are located on the mouths of Sharavathi and Nethravathi Rivers.

Based on the shale-normalized REE patterns Nath et al. (1997) has suggested that the shelf sediments off Karwar are derived either from the adjoining Archaean land masses or from distal Indus source. The clay minerals in the inner shelf are derived from Archaean gneissic sources (Nair et al. 1982). Certain accessory minerals have important role than clay minerals in controlling the REE distribution. Zircon controls the distribution of REE in the 0.1–2 μm fraction (Francesco Cavalcante et al. 2014).

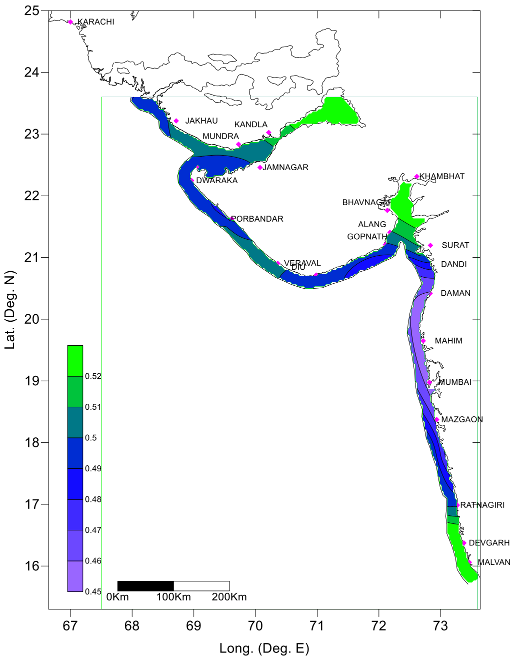


Fig. 4.15 Contour Map showing distribution of Thulium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

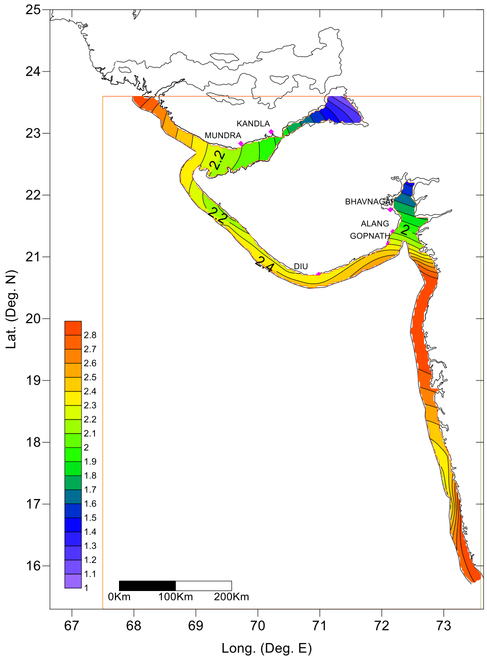
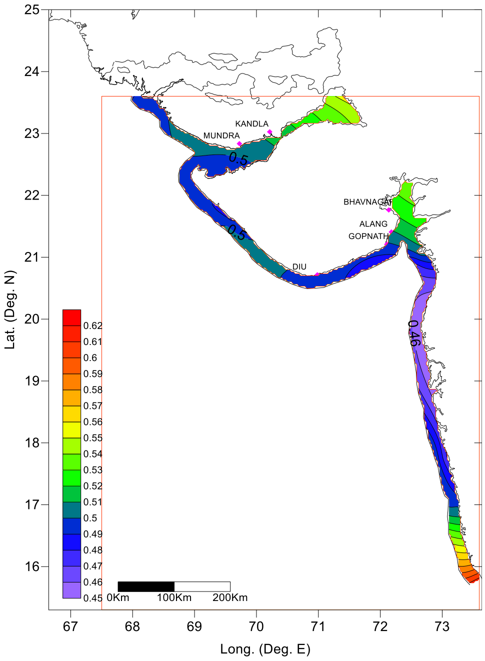


Fig. 4.16 Contour Map showing distribution of Ytterbium in the surface sediments within the inner shelf off Gujarat and Maharashtra.

Generally clayey silt/silty clay characterize the sediment texture in the shelf off Honavar where REE incidence is rather low (<75 mg. kg^{-1}). Sharavathi River could be bringing in sediment that has a diluting effect on REE, whereas Kali River which debouches near Karwar could be introducing REE into the shelf, through heavy minerals, though in small concentration as the incidence is 125 to 165 mg. kg^{-1}. Between Bhatkal and Mangalore the incidence of REE varies between 150 mg. kg^{-1} and 165 mg. kg^{-1} with lower values in the deeper part of the inner shelf and higher values close to the shallower inner shelf. South of Mangalore again there is another zone of low incidence of 45mg. kg^{-1} to 125 mg. kg^{-1}. Nethravathi River near Mangalore does not seem to have much influence on the distribution of REE in the nearby shelf sediments. No clear relationship can be observed between the incidence of REE and the texture of shelf sediments.



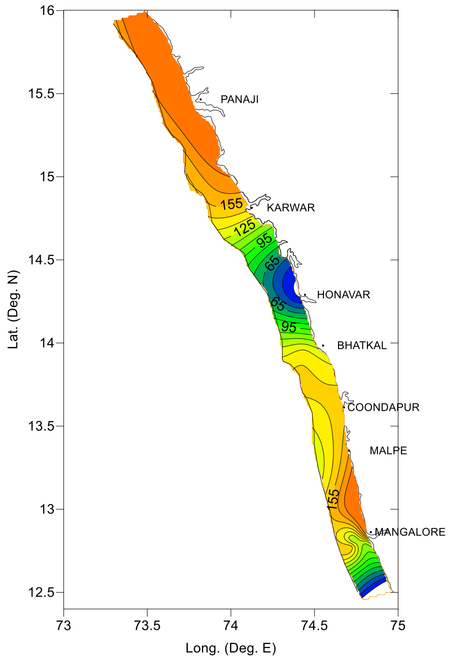


Fig. 4.17 Contour Map showing distribution of Lutetium in the surfacesediments within the inner shelf off Gujarat and Maharashtra.

Fig. 4.18 Contour Map showing distribution of ΣREE in the surface sediments within the inner shelf off Goa and Karnataka.

4.5 Distribution of LREE in the Surface Sediments off Goa and Karnataka coasts

LREE vary between 20.54 mg. kg^{-1} and 155.05 mg. kg^{-1} with an average content of 105.45 mg. kg^{-1} and a SD of 41.27. Its distribution is shown in Fig. 4.19 as contour map. High content is observed between Panaji and Karwar and also north of Mangalore. The sector between Malpe and Bhatkal show moderate LREE content. The inner shelf off Honnavar and south of Mangalore contain lowest LREE. There is a decrease in LREE from near to offshore. Off Goa the inner shelf sediment shows a consistent concentration of 140 mg. kg^{-1} to 160 mg. kg^{-1} of LREE with a gentle decrease towards offshore. From Karwar to Bhatkal there is a gradual lowering of the incidence of LREE from 120 mg. kg^{-1} to 20 mg. kg^{-1}. The lowest concentration is in the shelf off the mouth of Sharavathi River. It shows a concentration of 120 mg. kg^{-1} to 130 mg. kg^{-1} off Coondapur. Between Coondapur and Mangalore the concentration is 160 mg. kg^{-1} close to the nearshore strip with a gradual drop in the deeper parts of the territorial waters.

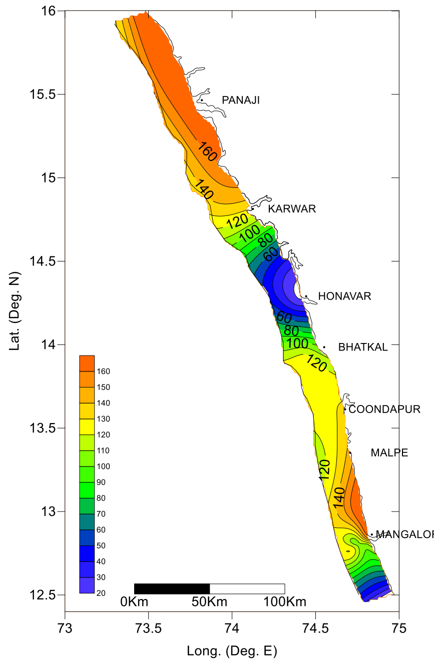


Fig. 4.19 Contour Map showing distribution of LREE in the surfacesediments within the inner shelf off Goa and Karnataka.

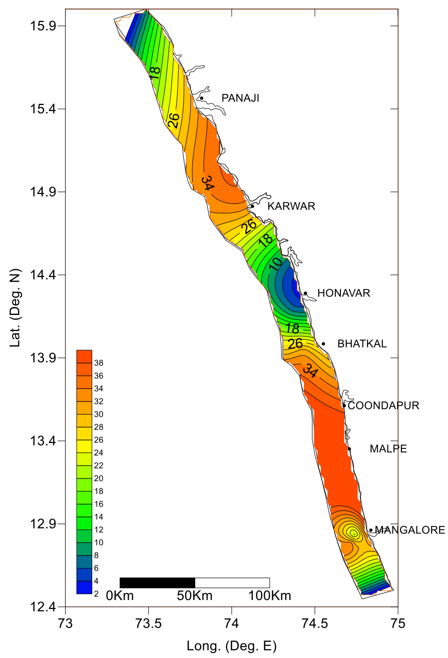


Fig. 4.20 Contour Map showing distribution of Lanthanum in the surface sediments within the inner shelf off Goa and Karnataka.

Lanthanum in surface sediments varies between 3.32 mg. kg^{-1} and 37.72 mg. kg^{-1} with an average of 25.66 mg. kg^{-1} and a standard deviation of 11.32 indicating low abundance. The distribution of the metal is given in Fig. 4.20. Lowest incidence of Lanthanum in the surface sediment is seen in the shelf off Honnavar which is <18 mg. kg^{-1}. The dominant sediment along this sector is clayey silt and silty clay. The distribution of La does not display any preference for sediment texture except that the low incidence is close to the area with influx from the rivers.

Cerium ranges from 6.04 mg. kg^{-1} to 75.82mg. kg^{-1} with an average content of 49.79 mg. kg^{-1} and a standard deviation of 21.26. Ce is low in the sediments off Sharavathi and Nethravathi River mouths. Even though Ce is the most abundant REE in the Earth's crust, its content is very low in the inner shelf sediments in this sector. Ce is very sensitive to Eh pH condition of the depositional environment. It will precipitate if oxidation condition prevails and if the environment is depositional, Ce enters into solution. Its distribution is given in Fig. 4.21. Cerium show very low concentration in the shelf sediments from Karwar to Bhatkal and again in the shelf south of Mangalore with a range of 15 mg. kg^{-1} to 55 mg. kg^{-1}. The influence of Sharavathi River and Nethravathi River cannot be ruled out in the lowering of Cerium content in the sediment due to dilution. Cerium shows an identical pattern of distribution as that of the total REE.

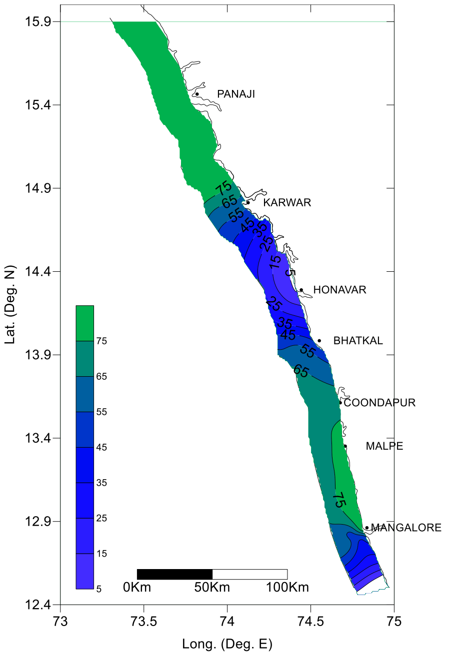


Fig. 4.21 Contour Map showing distribution of Cerium in the surface sediments within the inner shelf off Goa and Karnataka.

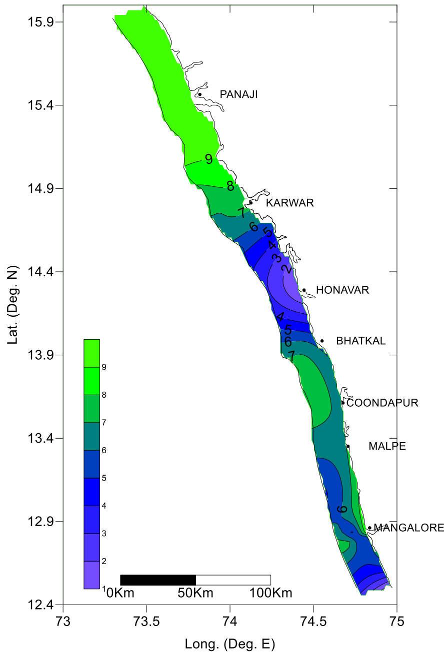


Fig. 4.22 Contour Map showing distribution of Praseodymium in the surface sediments within the inner shelf off Goa and Karnataka.

Fig. 4.22 shows the contour distribution of Praseodymium. Pr shows variation between 1.41 mg. kg^{-1} and 8.13 mg. kg^{-1} with a mean of 5.74 and SD of 2.17 suggesting its insignificant content in the shelf sediments. It is showing relatively high uniform content all along Goa shelf and also south of it till Karwar. Like other LREE, this metal also shows low abundance off Sharavathi and Nethravathi river mouths. Except for a minor increase from 6 mg. kg^{-1} to 7 mg. kg-

[1] off Coondapur, the entire shelf off Karnataka is poor in the incidence of Pr and it shows a consistency at 8 mg. kg^{-1} in the entire length of the inner shelf off Goa coast. The slightly higher, though negligible incidence of Pr is in association with the finer sediment in the shelf off Goa coast. Its incidence in the somewhat coarser sediments off two rivers Sharavathi and Nethravathi is lowest at 2 to 4 mg. kg^{-1}.

Neodymium in sediment show variation from 6.97 mg. kg^{-1} to 26.01 mg. kg^{-1} and its distribution is shown in Fig. 4.23.

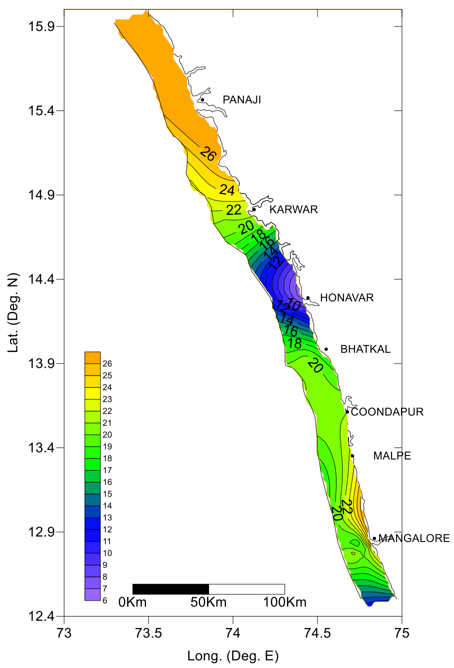


Fig. 4.23 Contour Map showing distribution of Neodymium in the surface sediments within the inner shelf off Goa and Karnataka.

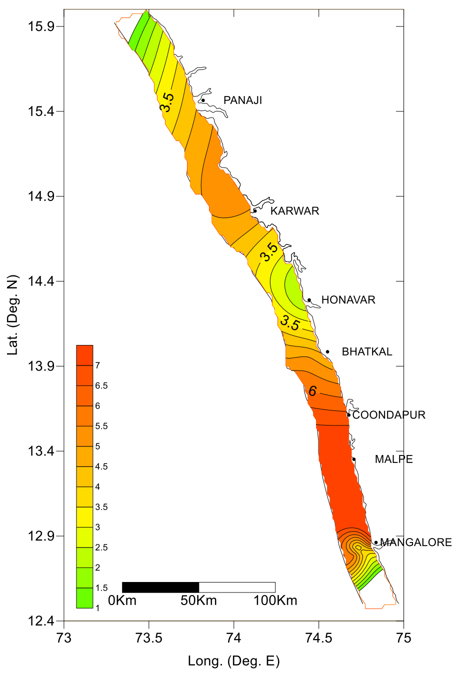


Fig. 4.24 Contour Map showing distribution of Samarium in the surface sediments within the inner shelf off Goa and Karnataka.

It has a mean of 18.86 mg. kg^{-1} and a SD of 5.43. The mean indicate presence of Nd in the shelf sediments in moderate proportion when compared to the low and high contents. Incidence of Neodymium is uniformly 26 mg. kg^{-1} in the entire stretch of the inner shelf off Goa within the TW zone. It records maximum content in the nearshore sediments north of Mangalore to Malpe and north Karwar. Off Honavar, Nd content is very low. While the low incidence of Neodymium (10 mg.

kg^{-1}) in the shelf off Honnavar can be attributed to the presence of dilution effect by influx from Sharavathi river, while the concentration goes up to 26 mg. kg^{-1} in the inner shelf off Nethravathi River, possibly because heavy mineral like monazite could be adding to the LREE.

Samarium content in the sediments is very low ranging between 2.16 mg. kg^{-1}and 6.23 mg. kg^{-1}with an average of 4.44 mg. kg^{-1} and SD of 1.23 following identical distribution pattern like rest of LREE (Fig. 4.24). Samarium is another LREE which is also very low in its presence in the surface sediments of inner shelf off Karnataka Goa coast. Its concentration is very low off Honavar and Sharavathi River mouth (<3 mg. kg^{-1}) and again off Mangalore and Nethravathi River mouth (<4 mg. kg^{-1}). It may not be sound to draw a relation between low incidence (<3.5 mg. kg^{-1}) of Samarium with the river inputs near the mouths of Sharavathi and Nethravathi rivers, since the concentration of Samarium in the sediments off Souparnika River shows no change. From the shelf off Bhatkal the concentration keeps steadily increasing from 4.5 mg. kg^{-1} to 7 mg. kg^{-1} near Coondapur and without any dilution maintains a consistent 7 mg. kg^{-1} up to Mangalore where it drops rapidly to 1.5 mg. kg^{-1}. In the northern sector, it keeps decreasing from 5 mg. kg^{-1} off Karwar to as low as 1 mg. kg^{-1} towards extreme north. Sediment from Mandovi River shows no influence on the concentration of Samarium.

Europium content is very low in the sediments along the inner shelf which show variation between 0.64 mg. kg^{-1} and 1.14 mg. kg^{-1} with an average of 0.96 mg. kg^{-1} and SD of 0.14. The presence of Europium is 0.95mg. kg^{-1} to 1.15mg. kg^{-1} in the inner shelf off Goa. It is very low off Sharavathi and moderately high north and south of Honnavar (Fig. 4.25). The negative Eu anomaly shown by the sediments possibly suggest a hinterland source rock depleted in Eu. Europium is the lowest in its concentration in the surface sediments in the inner shelf, among all the light REE. Its concentration goes down to 0.5 mg. kg^{-1} off Honnavar and Sharavathi River mouth. But it shows above 1.1 mg. kg^{-1} in the inner shelf off Mangalore and Nethravathi River.

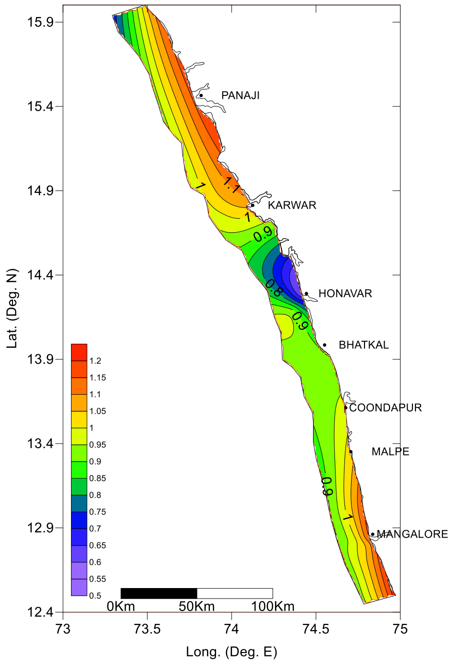


Fig. 4.25 Contour Map showing distribution of Europium in the surfacesediments within the inner shelf off Goa and Karnataka.

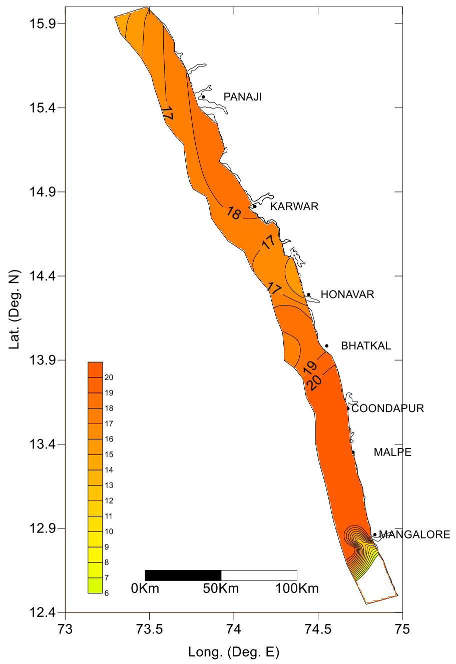


Fig. 4.26 Contour Map showing distribution of HREE in the surface sediments within the inner shelf off Goa and Karnataka.

4.6 Distribution of HREE in the Surface Sediments off Goa and Karnataka coast

HREE content too is low along this sector when compared to that of the inner shelf sediments from Kerala. The lowest content is 11.96 mg. kg^{-1} and the highest is 19.72 with an average of 17.01 mg. kg^{-1} signifying almost uniform presence of the metal in the sediments. The SD of 2.76 also suggests small variation from the mean content of the metal in the sediments. HREE incidence varies from 16 mg. kg^{-1} to 18 mg. kg^{-1} in the shelf off Goa, with gentle increase from north to south by 3 mg. kg^{-1} (Fig. 4.26). Then the concentration level drops from 18 mg. kg^{-1} to 15 mg. kg^{-1} off the mouth of Sharavathi River off Honnavar. The stretch of shelf off Honnavar to Bhatkal shows a variation from 15mg. kg^{-1} to 20 mg. kg^{-1}. From Coondapur to Mangalore it shows a uniform distribution of 20 mg. kg^{-1} along the entire length of the inner shelf. However, in the southern extreme there is a steep drop in the concentration of HREE from Mangalore to its south near Kerala border.

The Gadolinium content is very low in sediments ranging between 3.14 mg. kg^{-1} and 6.62 mg. kg^{-1} with an average of 5.04 mg. kg^{-1} and SD of 1.15. The distribution of the metal is given in Fig. 4.27. The incidence of Gd shows a gradual drop from 6.7 mg. kg^{-1} off Panaji in Goa to 3.2 mg. kg^{-1} off Honnavar. Further south the concentration of Gadolinium increases to 6.7 mg. kg^{-1} off Malpe and then it maintains a consistent 6.7 mg. kg^{-1} in the surface sediment up to Mangalore. There is a rapid drop from 6.7 mg. kg^{-1} to 0.7 mg. kg^{-1} immediately south of Mangalore.

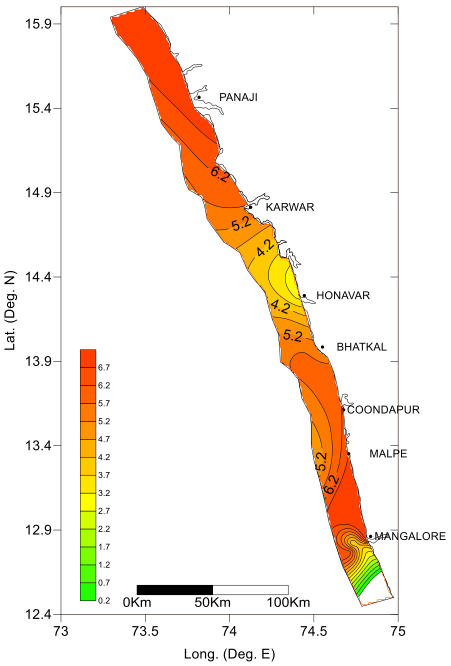


Fig. 4.27 Contour Map showing distribution of Gadolinium in the surface sediments within the inner shelf off Goa and Karnataka.

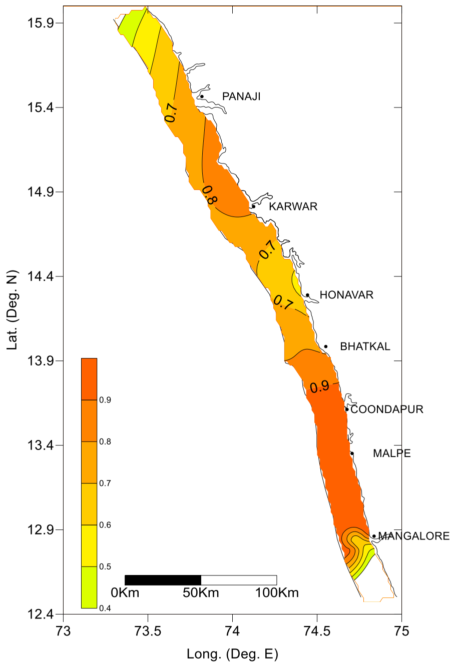


Fig. 4.28 Contour Map showing distribution of Terbium in the surface sediments within the inner shelf off Goa and Karnataka.

The distribution of this HREE shows influence of Sharavathi as well as Nethravathi Rivers. At the same time the influx of Mandovi and Souparnika Rivers have no impact on the concentration of Gadolinium in the inner shelf sediments.

Terbium content is negligibly low in the surface sediments which show variation from 0.58 mg. kg^{-1} to 0.88 mg. kg^{-1}. The average content of Tb in sediments from the inner shelf is 0.75 mg. kg^{-1} and the SD is 0.11. The distribution of Tb in the surface sediments of inner shelf shows a gradual increase from 0.4 mg. kg^{-1} in the northern limit of Goa's inner shelf to 0.8 mg. kg^{-1} in the inner shelf between Panaji and Karwar (Fig. 4.28). From Karwar to Honavar there is a gradual drop to 0.6 mg. kg^{-1} and then it increases to 0.9 mg. kg^{-1} between Bhatkal and Coondapur. Almost like the distribution of Sm, the Tb concentrations maintain a level of 0.9 mg. kg^{-1} to further south up to Mangalore from where there is a rapid drop from 0.9 mg. kg^{-1} to 0.4 mg. kg^{-1} within a short distance towards south along the inner shelf.

Dysprosium ranges between 3.24 mg. kg^{-1} and 5.01 mg. kg^{-1} and the average content in sediment is 4.42 mg. kg^{-1}. The SD of 0.63 suggests an almost uniform distribution of this metal in the surface sediments. From the northern limit of the inner shelf off Goan coast to Mangalore in the south, the variation in the incidence of Dy in the shelf sediment is from 4 mg. kg^{-1} to 5 mg. kg^{-1} which amounts to a uniform distribution for a long stretch of the inner shelf (Fig. 4.29). For the entire length of Goan inner shelf Dy shows an incidence of 4.5 mg. kg^{-1} plus. There is a very negligible drop of 0.5 mg. kg^{-1} in the incidence of Dy between Karwar and Honavar. Again in the stretch from Bhatkal to Coondapur, the concentration level decreases from 5 mg. kg^{-1} to 3.5 mg. kg^{-1}. Like Sm, Tb and Gd, Dy concentration drops rapidly from 4 mg. kg^{-1} to 0.5 mg. kg^{-1} in the southern tip of the Karnataka shelf. Only sediments from Nethravathi River show some impact in the form of dilution of the element distribution in the inner shelf sediment. Sediment inputs from other rivers do not seem to have any significant impact on its distribution in the surface sediments.

Holmium content is very low and ranges from 0.57 mg. kg^{-1} to 1.05 mg. kg^{-1}. The average content in sediments is 0.86 mg.kg^{-1} and the SD is 0.15. Incidence of Ho in the surface sediments of the inner shelf is around 0.86 mg. kg^{-1} on an average and its variation from 0.57 mg. kg^{-1} to 1.05 mg. kg^{-1} is not noticeable (Fig. 4.30). The distribution pattern is almost similar to that of Dy. Its incidence is uniformly at 1 mg. kg^{-1} for the entire stretch of Goa from Karwar to Bhatkal except for a negligible drop of 0.1 mg. kg^{-1} it retains 1mg. kg^{-1} level even up to Mangalore. Though between Bhatkal and Coondapur there is gradual drop towards deeper stretch of the inner shelf by 0.2 mg. kg^{-1} only. Only Nethravathi seems to display some impact on its distribution otherwise it is practically uniform from north (Goa) to immediate north of Mangalore, in the inner shelf.

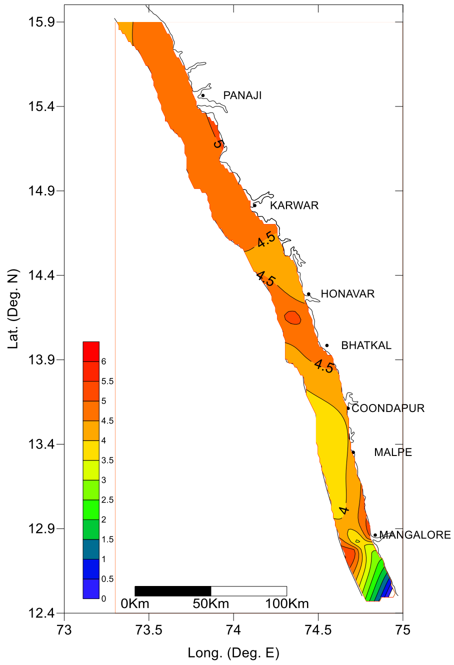


Fig. 4.29 Contour Map showing distribution of Dysprosium in the surface sediments within the inner shelf off Goa and Karnataka.

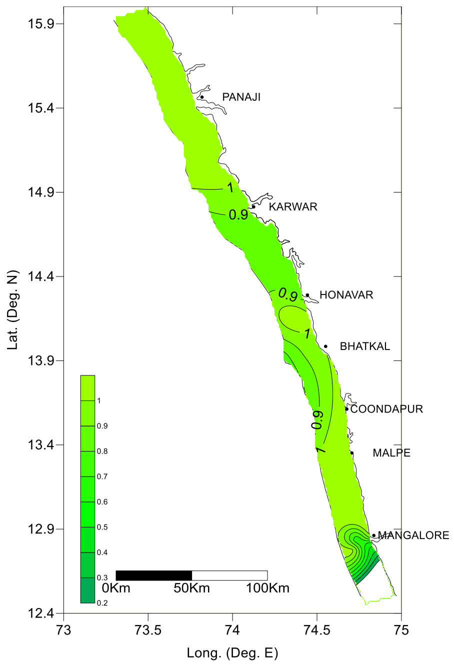


Fig. 4.30 Contour Map showing distribution of Holmium in the surface sediments within the inner shelf off Goa and Karnataka.

Erbium shows variation between 1.63 mg. kg^{-1} and 3.21 mg. kg^{-1} with an average of 2.49 mg. kg^{-1} and SD of 0.49. It is present in small amount in the nearshore sediments all through Goa and Karnataka inner shelf (Fig. 4.31). Incidence of Erbium in the surface sediment of the inner shelf is also less than that of Dy with an average of only 2.49 mg. kg^{-1}. Entire inner shelf stretch off Goa uniformly displays a concentration of 3.1mg. kg^{-1} of Er. It remains between 2.6 mg. kg^{-1} and 3.1 mg. kg^{-1} for the entire nearshore zone from Karnataka north to Malpe in the south. It shows a gradual drop from 3.1 mg. kg^{-1} to 2.6 mg. kg^{-1} orthogonally to the shoreline towards deeper part of the inner shelf off Karwar and Coondapur. Like in all the case of all other HREE there is a rapid drop in the incidence of Erbium from Mangalore to further south, which ranges from 3.1 mg. kg^{-1} to 0.1 mg. kg^{-1}.

Thulium content is extremely low in surface sediments which ranges from 0.23 mg. kg^{-1} to 0.5 mg. kg^{-1} with an average of 0.45 mg. kg^{-1} and SD of 0.09. Its content is slightly more between Bhatkal and Mangalore and also off Karwar (Fig. 4.32). Incidence of Tm in the surface sediment is lowest (<0.3 mg. kg^{-1}) in the extreme north off northern Goa and extreme south off south of Mangalore. In between for the entire stretch from Panaji to Mangalore its level of concentration remains between 0.4 to 0.5 mg. kg^{-1}. Bhatkal to Mangalore its incidence is consistent at 0.4 mg. kg^{-1} to 0.5 mg. kg^{-1} along and across the length of the inner shelf.

The low incidence of 0.4 mg. kg^{-1} of Tm off Honavar could be due to sediments input from Sharavathi River, such smallscale lowering need not require dilution by sediment. The rapid drop of incidence of Thulium in the surface sediments of the inner shelf near southern Mangalore shelf can be attributed to dilution by the influx of sediment through Nethravathi River into the shelf.

Ytterbium in sediments is low between 1.57 mg. kg^{-1} and 3.31 mg. kg^{-1} with average content of 2.54 mg. kg^{-1} and SD of 0.57. Incidence of Yb is similar to the concentration level of Er. Er has an average level of 2.49 mg. kg^{-1} against 2.54 mg. kg^{-1} of Yb. It shows a low concentration of 2.5 mg. kg^{-1} to 3.0 mg. kg^{-1} from Panaji to south of Karwar (Fig. 4.33). Off Honavar it maintains a level of 3 pm. Bhatkal to Mangalore the concentration of Ytterbium in the surface sediment rises from 3 mg. kg^{-1} to 3.5 mg. kg^{-1} off Malpe and drops down to 2.5 mg. kg^{-1} in the shelf near Mangalore. Like other HREE described above there is rapid drop from 2.5 mg. kg^{-1} to 1 mg. kg^{-1} within a very short stretch of the shelf southward of Mangalore. Off Sharavathi there is a mild drop in the incidence of Ytterbium in the deeper parts of Inner shelf off Karwar north and Bhatkal only.

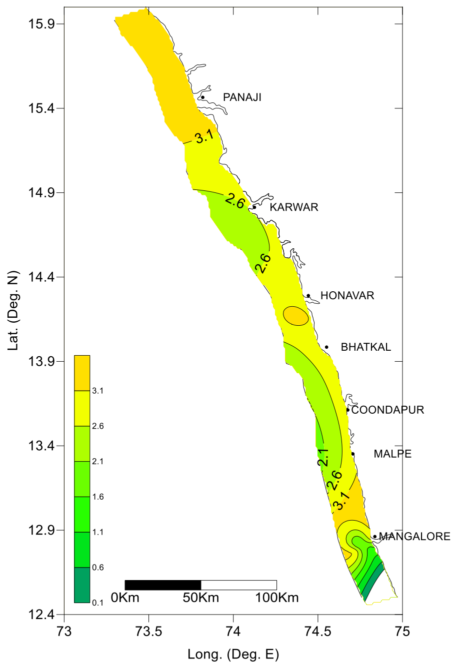


Fig. 4.31 Contour Map showing distribution of Erbium in the surface sediments within the inner shelf off Goa and Karnataka.

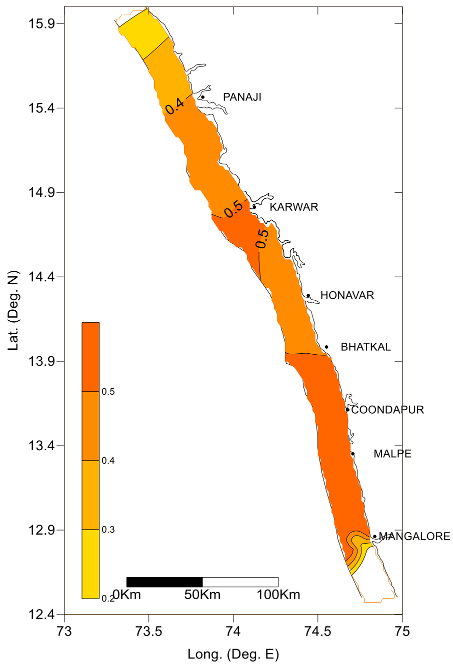


Fig. 4.32 Contour Map showing distribution of Thulium in the surface sediments within the inner shelf off Goa and Karnataka.

Lutetium is present is extremely low amount with the lowest of 0.26 mg. kg^{-1} and the highest of 0.53 mg. kg^{-1}. The average content is 0.46 mg. kg^{-1} and the SD is 0.10. The incidence of Lu in the shelf sediments within the inner shelf is as low as that of Thulium. Entire inner shelf off Goa shows a higher incidence of 0.5 mg. kg^{-1} to 0.6 mg. kg^{-1} with higher concentration in the northern sector (Fig. 4.34). Off Karwar the concentration level goes down to 0.5 mg. kg^{-1}. From immediate south of Karwar to Bhatkal it shows a uniform incidence of 0.5 mg. kg^{-1}. From Bhatkal to Mangalore it is 0.5 mg. kg^{-1} along the nearshore zone but gradually a drop in the incidence of Lutetium is seen in the deeper parts of the inner shelf when it goes down to 0.4 mg. kg^{-1}. Like all the HREE Lutetium also shows rapid decrease of its content in the surface sediments, as it goes down from 0.5 mg. kg^{-1} to 0.1 mg. kg^{-1} in the extreme south. Sharavathi and Nethravathi Rivers indicate some mild and strong influence respectively on the incidence of Lutetium in the inner shelf sediments.

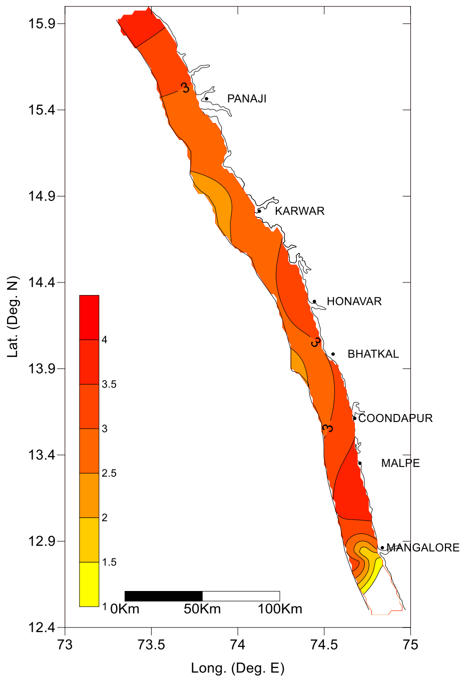


Fig. 4.33 Contour Map showing distribution of Ytterbium in the surface sediments within the inner shelf off Goa and Karnataka.

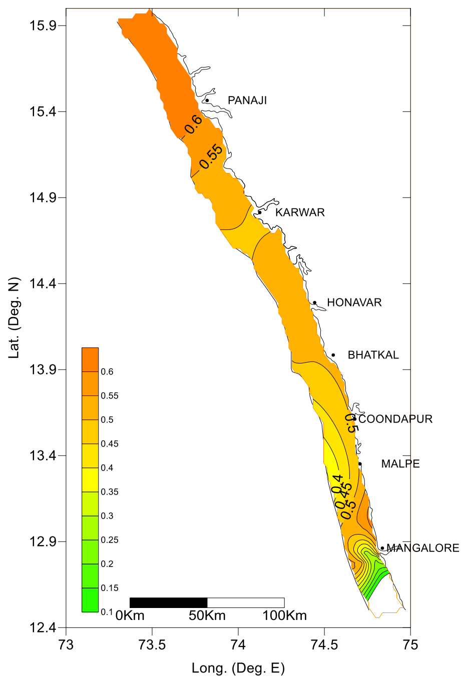


Fig. 4.34 Contour Map showing distribution of Lutetium in the surface sediments within the inner shelf off Goa and Karnataka.

4.7 Distribution of REE in Surface Sediments off Kerala Coast

The sediment distribution map of the inner shelf, off Kerala coast shows the domination of sand in the shallow seafloor south of Quilon as well as in the deeper part of inner shelf from Vizhinjam to Ponnani. Rest of the seafloor adjoining the coast is mostly covered by silty clay and clayey silt, from north of Quilon to Kasaragod. REE in the inner shelf sediments varies between 9.15 mg. kg^{-1} and 319.66 mg. kg^{-1} and their distribution is depicted in Fig. 4.35 as contour map. The sediments occurring between Ponnani and Vizhinjam show higher REE (>200 mg. kg^{-1}), whereas moderate to low REE is observed in the northern sector between Ponnani and Kasaragod. REE is very high in the nearshore sediments between Alappuzha and Vizhinjam. Study by Siby et al. (2013) also has indicated moderately high REE concentrations in the sediments off Kollam and Kochi. REE in moderately high proportion in the shelf sediments along southern Kerala was also reported by Anil Kumar et al. (2016) and Jayaprakash et al. (2016).

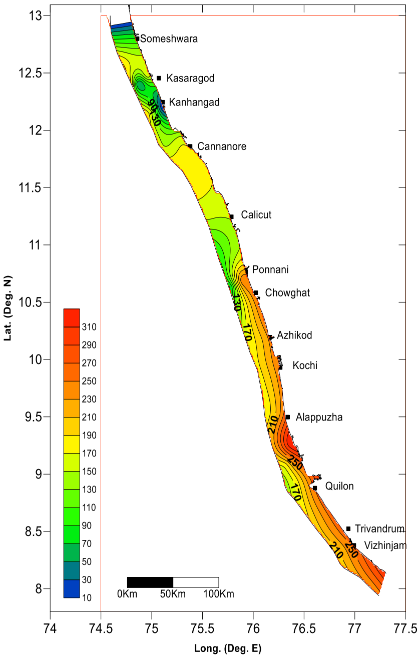


Fig. 4.35 Contour Map showing distribution of ΣREE in the surface sediments within the inner shelf off Kerala.

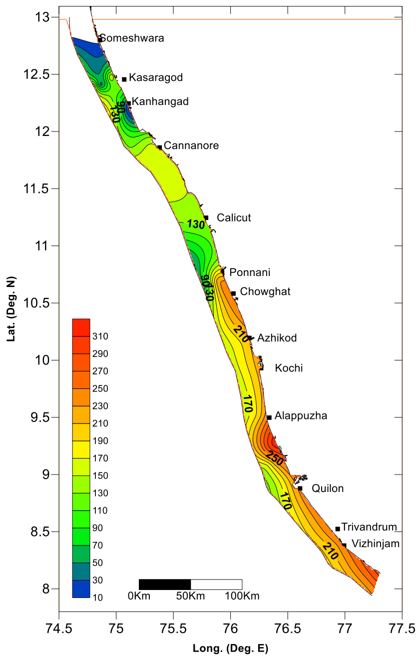


Fig. 4.36 Contour Map showing distribution of LREE in the surface sediments within the Inner shelf off Kerala.

4.8 Distribution of LREE in Surface Sediments off Kerala Coast

LREE in surface sediments within the Territorial Waters off Kerala ranges between 5.61 mg. kg^{-1} and 306.31 mg. kg^{-1} and its distribution is shown in Fig. 4.36. The contour map suggests high LREE in sediments south of Ponnani to Vizhinjam and moderate to low LREE north of Ponnani following the similar trend of total REE. Highest LREE is recorded off Alappuzha and the lowest off Kasaragod in the north. The sector between Kozhikode and Kannur show moderately high LREE. South of Ponnani the contour distribution pattern follows a trend nearly parallel to the presentday beach. The REE content is gradually decreasing from land to offshore.

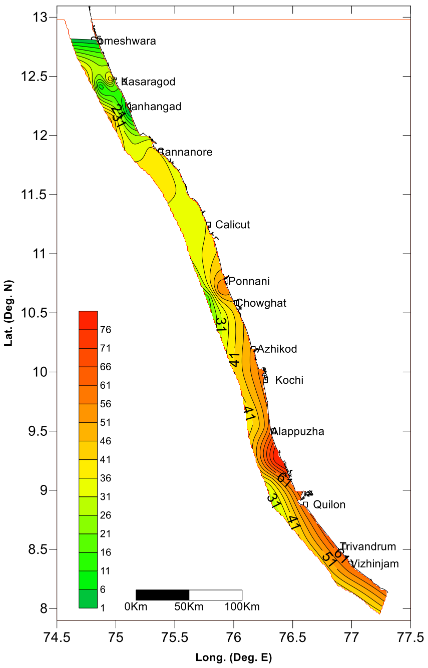


Fig. 4.37 Contour Map showing distribution of Lanthanum in thesurface sediments within the inner shelf off Kerala.

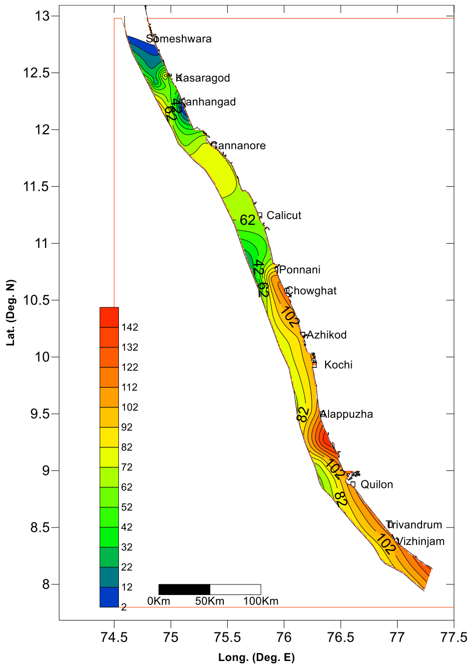


Fig. 4.38 Contour Map showing distribution of Cerium in the surface sediments within the inner shelf off Kerala.

Lanthanum ranges between 1.08 mg. kg^{-1} and 78.57 mg. kg^{-1} with a standard deviation (SD) of 17.55 (Fig.4.37). The sediment sample collected off Kayamkulam shows the highest concentration of La whereas the sample from Karingote river mouth, south of Kanhangad, has analyzed the lowest. The sector between Ponnani and Vizhinjam shows high concentration of La, whereas the Ponnani-Kannur sector shows moderate content of La.

Cerium content ranges from 2.16 mg. kg^{-1} to 143.21 mg. kg^{-1} and like La it also shows highest concentration off Ponnani-Vizhinjam sector (Fig. 4.38). The average content of this metal in sediments is 69.09 mg. kg^{-1} and the standard deviation (SD) is 31.34. The very high SD suggests considerable variation in the Ce content in sediments. The lowest concentration of Ce is recorded in the offshore segment between Kasaragod and Kanhangad. The contour distribution indicates higher abundance of this element along southern Kerala coast between

Ponnani and Vizhinjam and lesser content north of Ponnani. Like La, Ce also shows moderate concentration between Ponnani and Kannur sector.

Praseodymium varies between 0.43 mg. kg^{-1} and 15.6 mg. kg^{-1} with a mean of 7.91 mg. kg^{-1} indicating its very low abundance in sediments (Fig. 4.39). The standard deviation of 3.55 suggests presence of this metal in all samples in a relatively uniform manner. Lowest content of Pr is recorded in the sediments off Someshwara. The shallow inner shelf off Kanhangad and the deeper inner shelf off Ponnani also show very low abundance of Pr. The trend observed in the contour pattern illustrates decrease in Pr in sediments from the coast towards the offshore all through Kerala.

Neodymium ranges from 1.56 mg. kg^{-1} in Karingote river mouth to 55.68 mg. kg^{-1} in the sediments off Kayamkulam (Fig. 4.40). It has an average content of 27.12 mg. kg^{-1} and the SD of 12.84 suggests fluctuation in its content in the surface sediments. The sector between Ponnani and Vizhinjam shows maximum content of Nd and peak concentration is observed off Alappuzha and Vizhinjam. Kannur-Ponnani sector shows moderate Nd and its lowest content is observed off Someshwara and Kanhangad. The sediments from the deeper part of inner shelf off Ponnani also show low Nd content.

Samarium varies between 0.32 mg. kg^{-1} and 10.28 mg. kg^{-1} with an average of 5.78 mg. kg^{-1}. The SD of 2.54 suggests its consistent presence in the inner shelf sediments. Sm shows higher concentration in the offshore sectors between Ponnani and Vizhinjam like that of most of other LREE (Fig. 4.41). Kasaragod-Kanhangad offshore sector shows the lowest content whereas Calicut-Kannur sector records moderate content of Sm. The contour pattern depicts a gradual decline in the Sm content from shallow to deeper areas across the shore.

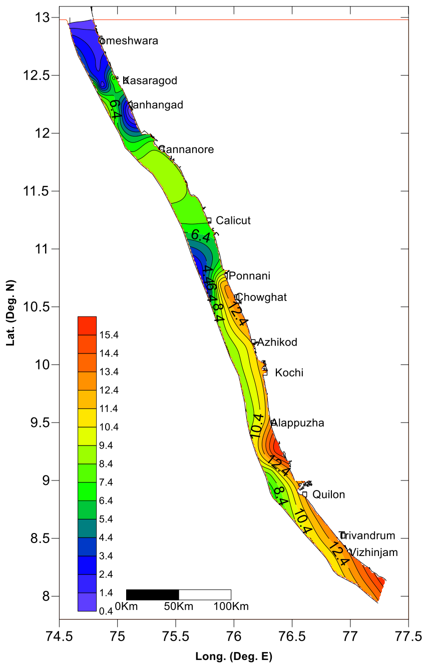


Fig. 4.39 Contour Map showing distribution of Praseodymium in the surface sediments within the inner shelf off Kerala.

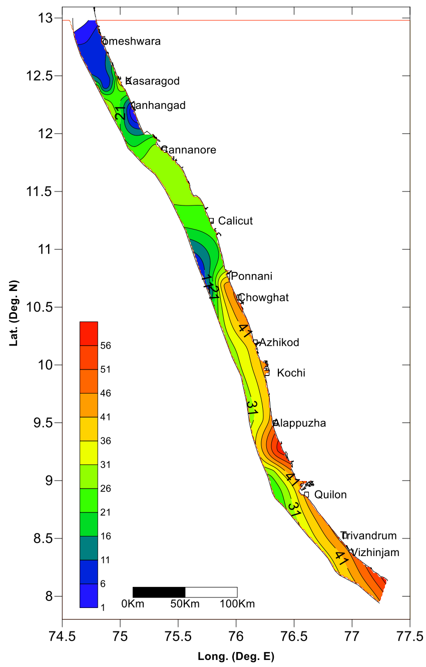


Fig. 4.40 Contour Map showing distribution of Neodymium in the surface sediments within the inner shelf off Kerala.

Europium is very low, ranging from 0.06 mg. kg^{-1} recorded in the Karingote river mouth to 2.97 mg. kg^{-1} in the Chandragiri river mouth (Fig. 4.42). The lowest Eu is in the sediments off Kasaragod-Kanhangad sector. Between Ponnani and Calicut too the Eu content is very low. Like other LREE, Eu is also relatively high off Ponnani-Vizhinjam sector.

4.9 Distribution of HREE in Surface Sediments off Kerala

Distribution pattern of HREE is shown in Fig. 4.43. Its content in the sediments is very low and ranges from 2.91 mg. kg^{-1} to 36.8 mg. kg^{-1}. The sector between Calicut and Quilon show higher content of HREE whereas the offshore between Kanhangad and Someshwara, south of Quilon and off Ponnani show very small HREE in sediments. Between Cannanore and Calicut, the heavy rare earths are relatively moderate.

Gadolinium varies from 0.58 mg. kg^{-1} in the Karingote river mouth to 11.89 mg. kg^{-1} in the Chandragiri river mouth respectively. The contour distribution maps of these metals are given in Fig. 4.44. The sediments off Ponnani-Alappuzha show relatively higher content of Gd. The sediments along the Kerala inner shelf show very low Gd content. Kasaragod-Kanhangad and north of Ponnani sectors show very low Gd in inner shelf.

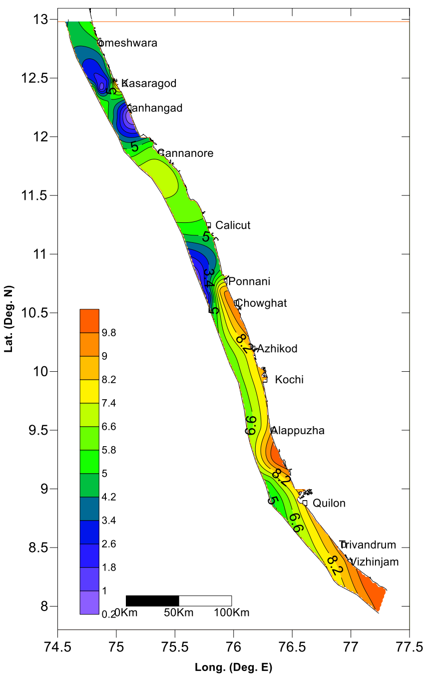


Fig. 4.41 Contour Map showing distribution of Samarium in the surface sediments within the inner shelf off Kerala.

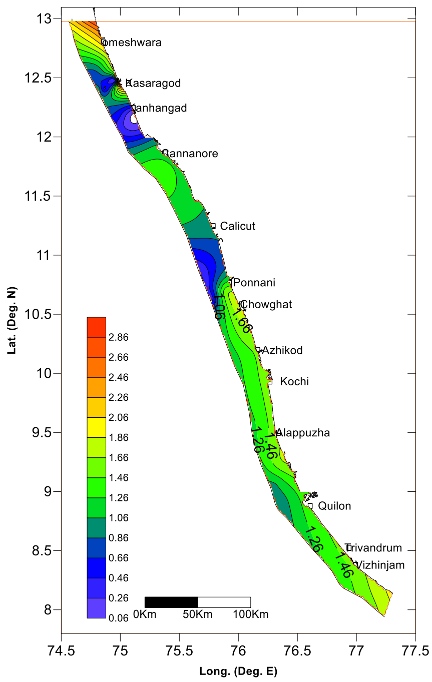


Fig. 4.42 Contour Map showing distribution of Europium in the surface sediments within the inner shelf off Kerala.

Distribution of Terbium is shown in Fig. 4.45. The content of this metal is very low along the entire Kerala inner shelf. Tb vary between 0.09 mg. kg^{-1} and 1.81 mg. kg^{-1} suggesting its very low content. The average content of 0.77 mg. kg^{-1} and SD of 0.35 again indicate the presence of this metal in relatively uniform manner in entire shelf sediments. Southern sector shows relatively higher content of Tb in sediments. Moderate content of 0.5 mg. kg^{-1} to 1 mg. kg^{-1} is observed in the Calicut-Cannanore sector.

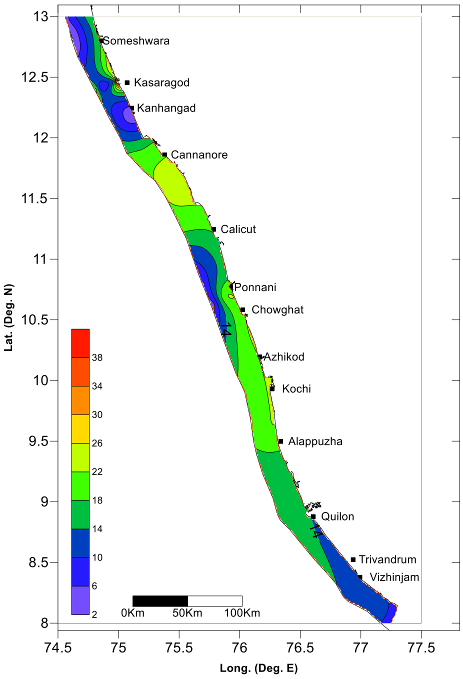


Fig. 4.43 Contour Map showing distribution of ΣHREE in surface sediments within the inner shelf off Kerala.

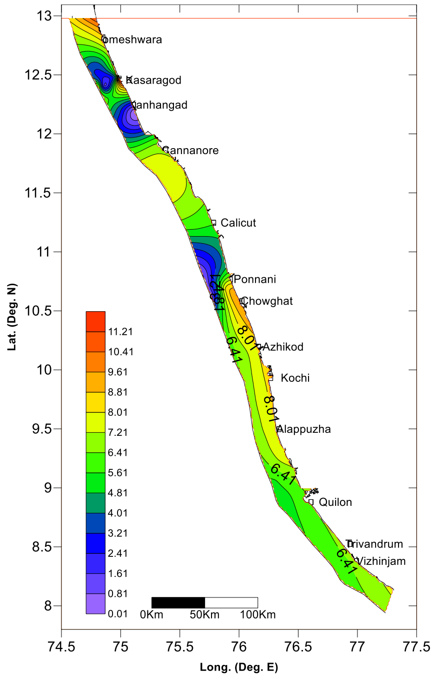


Fig. 4.44 Contour Map showing distribution of Gadolinium in surface sediments within the inner shelf off Kerala.

Lowest Dysprosium content of 0.77 mg. kg^{-1} is from the sediment sample off Bharatapuzha mouth whereas the highest of 10.03 mg. kg^{-1} is from Chandragiri river mouth. Sectors such as Kasaragod-Kanhangad, Alappuzha-Trivandrum and Ponnani recorded lower Dy (Fig. 4.46). The Alappuzha-Vizhinjam sector has very low Dy and the inner shelf between Alappuzha and Ponnani and between Calicut and Cannanore has relatively high Dy in sediments. The contour distribution pattern of this metal show discontinuity in its content in the sediments.

Ho in the sediments ranges from 0.18 mg. kg^{-1} in the Karingote river mouth to 1.96 mg. kg^{-1} in Chandragiri river mouth. Low concentration of Ho is found off Kasaragod-Kanhangad and Alappuzha-Trivandrum sectors. Fig. 4.47 shows the surface distribution of Ho in sediments.

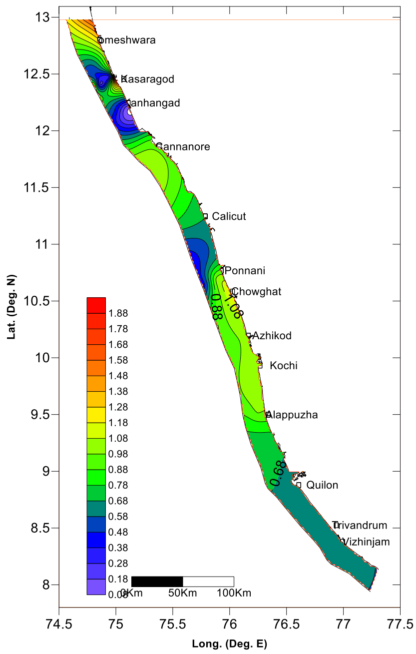


Fig. 4.45 Contour Map showing distribution of Terbium in surface sediments within the inner shelf off Kerala.

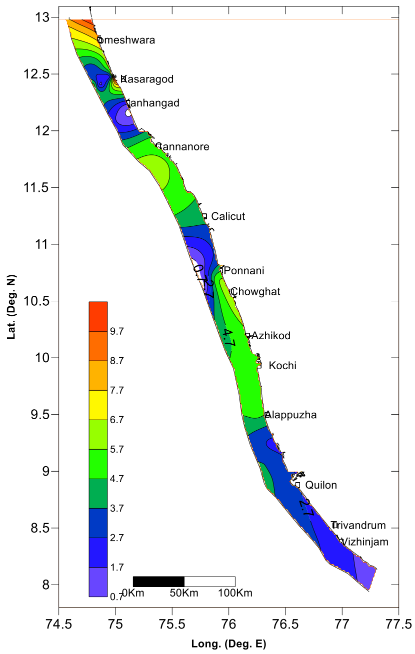


Fig. 4.46 Contour Map showing distribution of Dysprosium in surface sediments within the inner shelf off Kerala.

Lowest Erbium content of 0.5 mg. kg^{-1} is from the sediment sample off Bharatapuzha mouth whereas the highest of 5.25 mg. kg^{-1} is from Chandragiri river mouth. Sectors such as Kasaragod-Kanhangad, Alappuzha-Trivandrum and Calicut-Ponnani recorded lower Er (Fig. 4.48). Relatively high Er is associated with sediments off Ponnani-Alappuzha and Calicut-Cannanore.

Thulium content is extremely low along the entire inner shelf and the sector between Cannanore and Vizhinjam show consistent presence of this metal. Lowest Tm of 0.13 mg. kg^{-1} is in the sample from Karingote river mouth and the maximum content of 0.79 mg. kg^{-1} is recorded in the Chandragiri river mouth. Its surface distribution is given in Fig. 4.49.

Highest ytterbium content of 4.41 mg. kg^{-1} is in Chandragiri sediments and lowest of 0.5 mg. kg^{-1} is associated with sediments from Bharatapuzha mouth. There is an inconsistency in the distribution of Yb with sectors such as Alappuzha-Vizhinjam, Ponnani-Calicut and Kanhangad-Kasaragod showing lowest content and Ponnani-Alappuzha and Calicut-Cannanore showing relatively higher content (Fig. 4.50).

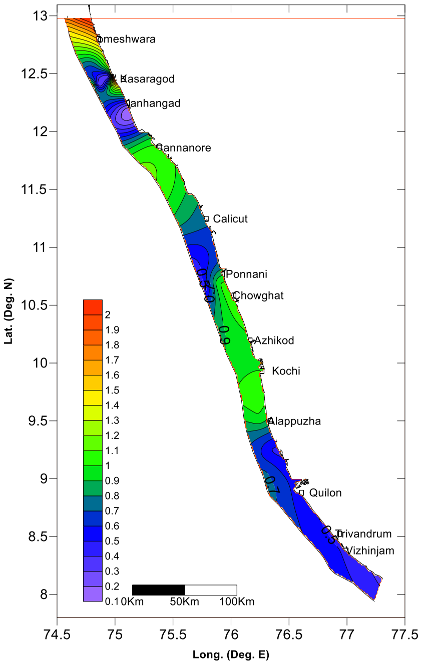


Fig. 4.47 Contour Map showing distribution of Holmiumin surface sediments within the inner shelf off Kerala.

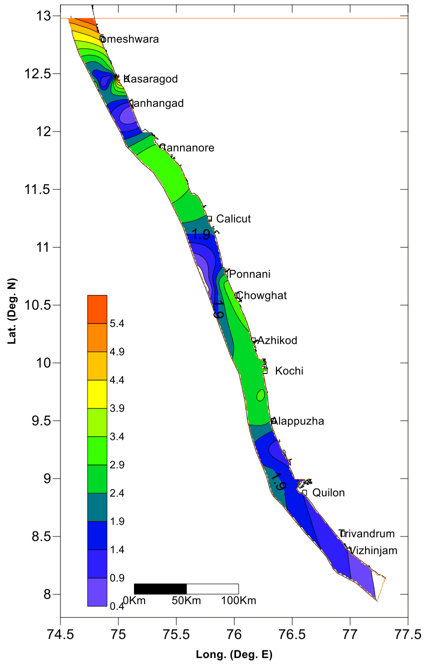


Fig. 4.48 Contour Map showing distribution of Erbium in surface sediments within the inner shelf off Kerala.

Lu ranges from 0.16 mg. kg^{-1} off Karingote river mouth to 0.66 mg. kg^{-1} off Chandragiri river mouth. Its content in sediments is extremely low all along Kerala coast. Fig. 4.51 shows the surface distribution of Lu in sediments. The sector between Cannanore to Vizhinjam, Lu content remains almost uniform with variation between 0.4 mg. kg^{-1} and 0.6 mg. kg^{-1}.

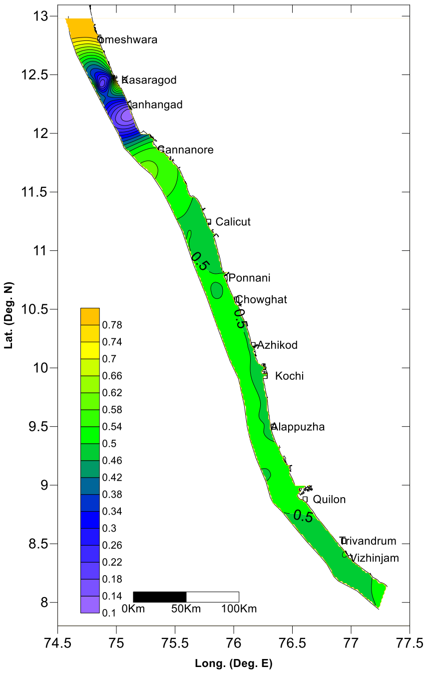


Fig. 4.49 Contour Map showing distribution of Thulium in surface sediments within the inner shelf off Kerala.

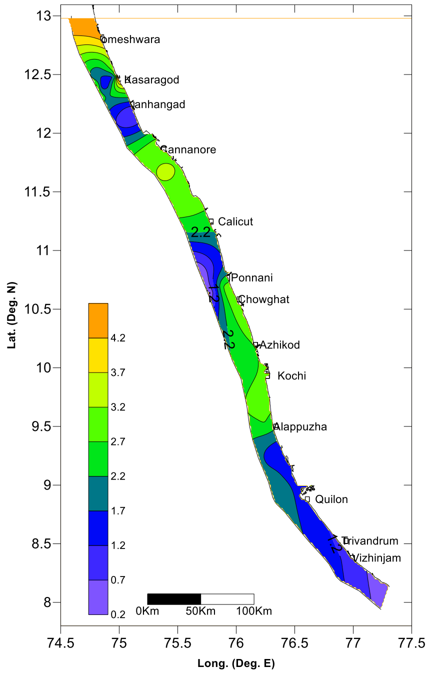


Fig. 4.50 Contour Map showing distribution of Ytterbium in surface sediments within the inner shelf off Kerala.

4.10 Comparison with Post Archaean Australian Shale (PAAS)

In order to compare the ΣREE in sediments with that of Post Archaean Australian Shale (PAAS), REE data of sediments along the Gujarat and Maharashtra inner shelf were normalized using PAAS (Fig. 4.52). The sediments in general show depletion in both LREE and HREE compared to PAAS. Samples collected off Murud and Ratnagiri in Maharashtra are showing enrichment in HREE.

Fig. 4.53 shows the comparison of ΣREE off Goa and Karnataka coast. All through the inner shelf the sediments are showing composition very much similar to that of PAAS with out any appreciable enrichment of depletion except in the sample collected off Netravathi River mouth where all the REE are showing relative depletion. LREE are showing depletion in the sediments from Sharavathi River mouth.

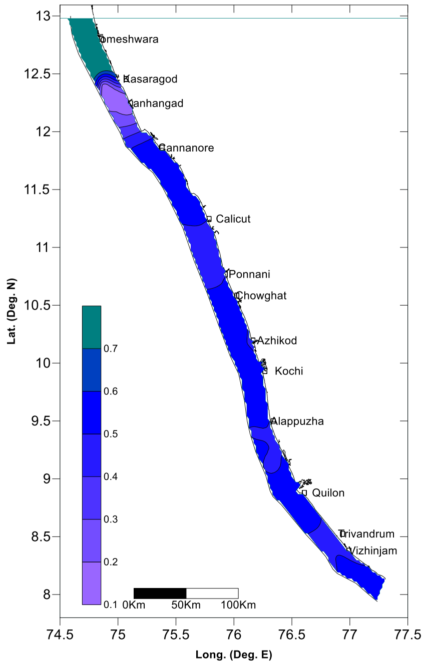


Fig. 4.51 Contour Map showing distribution of Lutetium in surface sediments within the inner shelf off Kerala.

PAAS data were compared with REE data of sediments from Kasaragod, Ponnani and Vizhinjam representing northern, central and southern inner shelf were normalized using PAAS (Fig. 4.54). The sediments from Vizhinjam (southern sector) and Ponnani (central sector) show enrichment ΣLREE compared to PAAS. There is a depletion in La, Ce and Pr in the shelf sediments from Kasaragod whereas other LREE are higher than PAAS. HREE is enriched in the central and northern sectors and depleted in the sediments off Vizhinjam compared to PAAS.

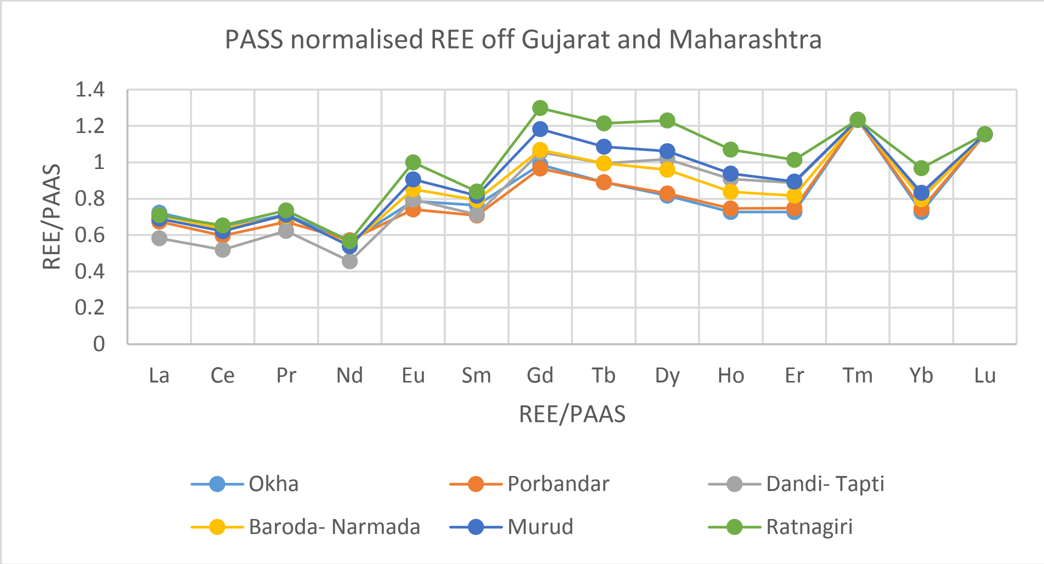


Fig. 4.52 PAAS normalized REE in the Surface Sediments off Gujarat and Maharashtra.

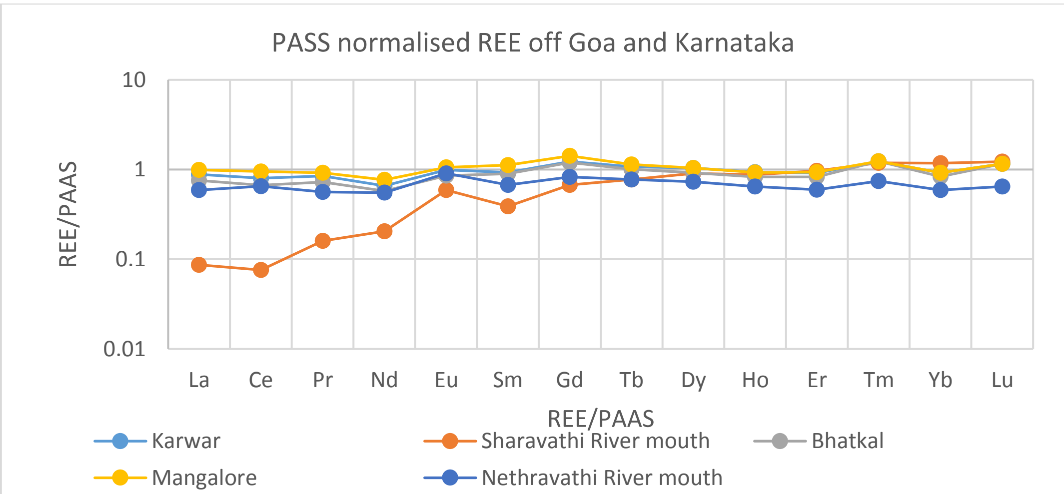


Fig. 4.53 PAAS normalized REE in the Surface Sediments offGoa and Karnataka.

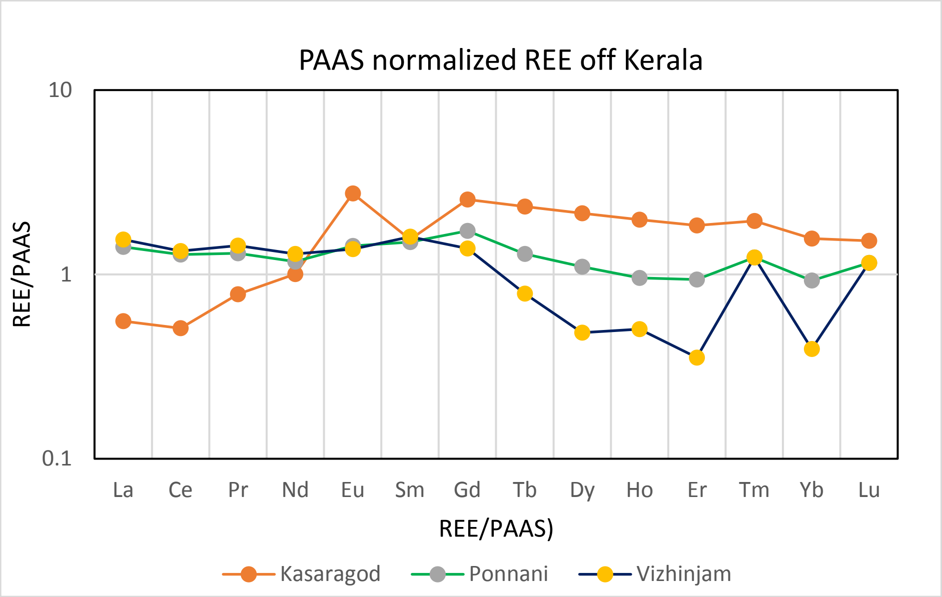


Fig. 4.54 PAAS normalized REE in the Surface Sediments off Kerala.

4.11 Conclusion

The hinterland geology of west coast is given in Fig. 4.55. The southern coastal stretch is covered by gneisses and granulites south of Goa, whereas Deccan basalt is the dominant lithology north of Goa up to Dwarka. A thin strip of Quaternary rocks margins the coastal stretch all along Saurashtra and Kutch consisting of miliolitic limestone. Total REE in the inner shelf sediments ranges from 9.15 mg. kg^{-1} to 319.66 mg. kg^{-1} (Fig. 4.56) with an average of 143.37 mg. kg^{-1} and SD of 55.88. Based on REE content in surface sediment, the entire west coast inner shelf is classified into four main sectors.

1. The high REE Sector along southern Kerala coast between Ponnani and Vizhinjam.
2. The moderately high sector between Ponnani in Kerala to Ratnagiri in Maharashtra and between north of Porbandar to Jakhau in Gujarat.
3. Low concentration sector between Ratnagiri in Maharashtra to Porbandar in Gujarat.
4. Very low concentration sector in the Gulf of Khambhat and Gulf of Kutch in Gujarat.

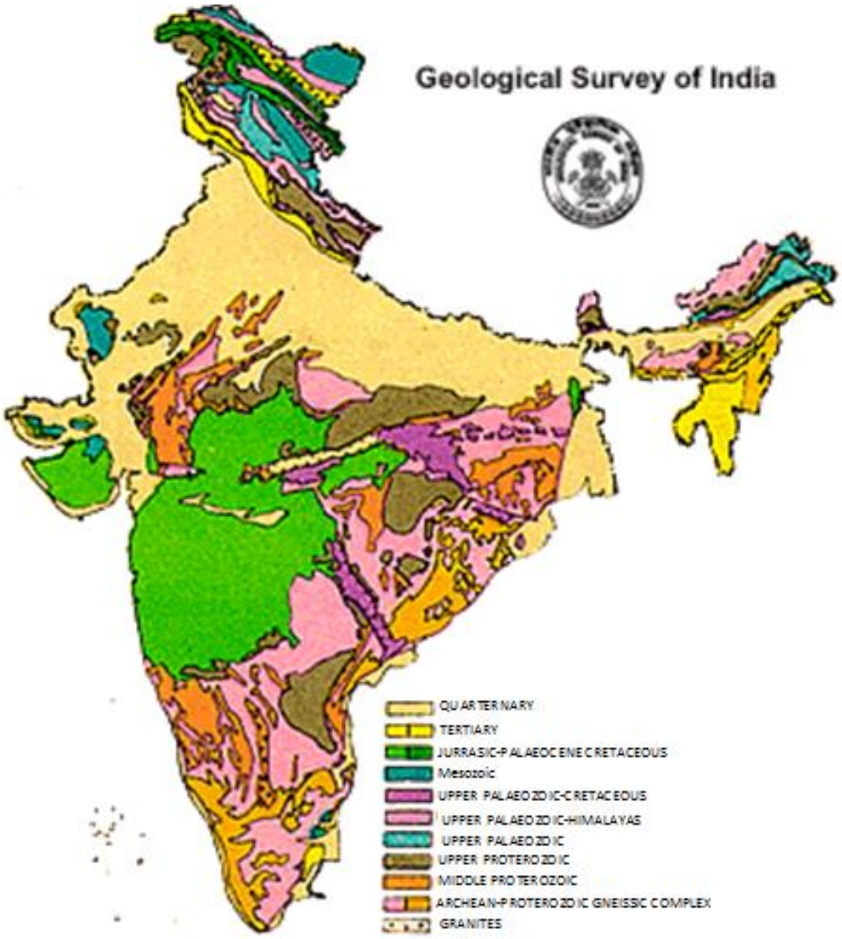


Fig.4.55 Generalized geological map of India (Source: www.portal.gsi.gov.in).

Total LREE in the inner shelf sediments ranges from 5.61 mg. kg^{-1} to 304.97 mg. kg^{-1} with an average of 126.57 mg. kg^{-1} and SD of 54.06. The distribution pattern of LREE follows the same trend as shown by REE, suggesting LREE as the principal component of the total REE in sediments (Fig. 4.57). The variation in the distribution patterns of both REE and LREE to a greater extent; appear to have a bearing on the hinterland geology. The sector between Goa and Kerala is mostly occupied by gneisses and charnockites, whereas, north of Goa to Surat and also the Saurashtra coast exposes Deccan trap basalt in the hinterland. The Kutch coast is covered by miliolitic limestone.

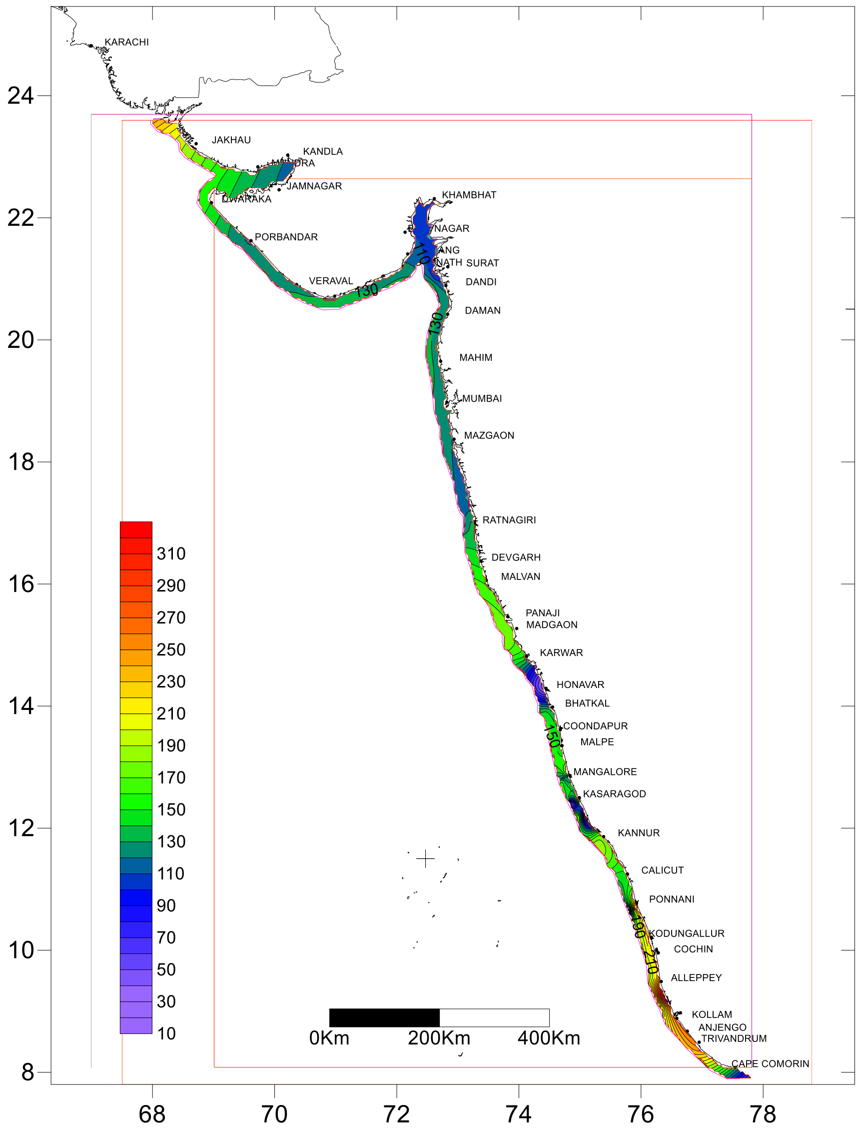


Fig. 4.56 Contour Map showing distribution of REE in the surface sediments within the inner shelf off West Coast of India.

The high and moderate REE sectors are seen between Ratnagiri in Maharashtra and Vizhinjam in Kerala. These sectors have Archaean and Pre-cambrian rocks represented by gneisses and charnockites. Study of the surface sediments from the western continental shelf of India by Siby et al. (2013) has shown Deccan basalt as the major source for sediments from Dwaraka to Goa and gneisses and granulites from Goa to Cape Comorin. Since REE present in terrigenous minerals are largely unreactive, they will be reflecting the signature of hinterland source rocks (Sholkovitz et al. 1994). In addition to the influence exerted by the petrology of hinterland source rocks in controlling the REE content of near shore sediments, other factors such as sediment texture and river discharges also govern their distribution in the west coast inner shelf. The seafloor covered with coarser sandy sediments, in general, are not locations for the enrichment of REE compared to the one covered with silt and clay. The fine, electronegative sediments have the ability to adsorb electropositive REE on their surfaces resulting in the enrichment of these metals.

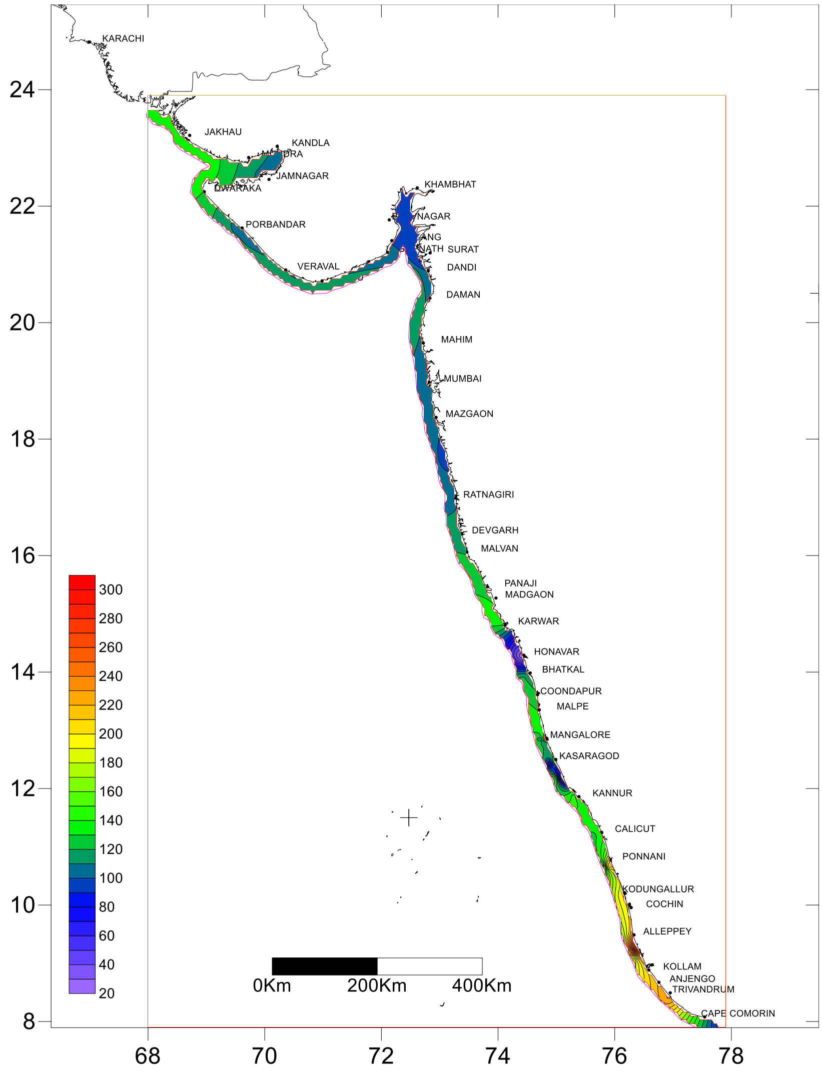


Fig. 4.57 Contour Map showing distribution of LREE in the surface sediments within the inner shelf off West Coast of India.

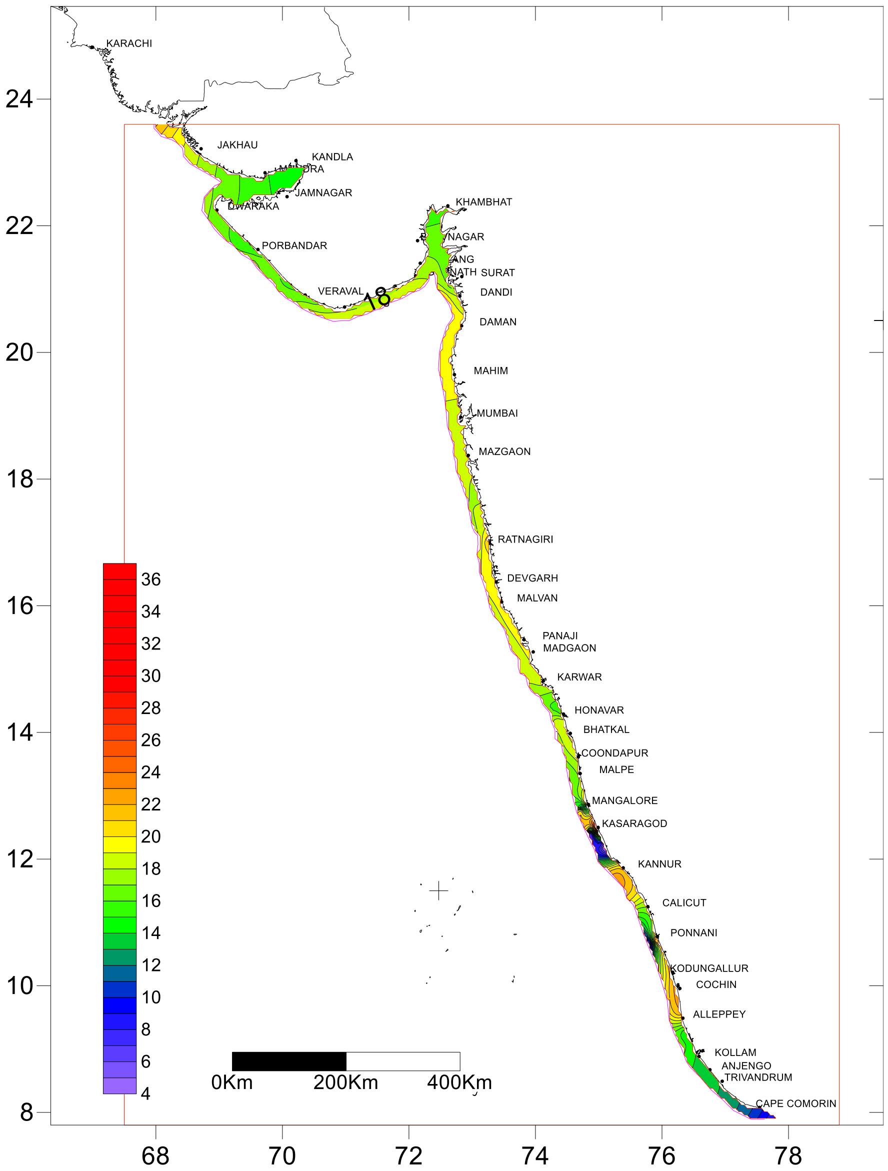


Fig. 4.58 Contour Map showing distribution of HREE in the surface sediments within the inner shelf off West Coast of India.

From the mineralogical point of view, REE are known to associate mostly with oxides, phosphates and silicates in marine sediments. The discharge of huge quantity of sediments by some of the major rivers debouching in to Arabian Sea appears to have caused dilution of the original REE regime. This is reflected in several locations such as off Nethravathi, Sharavathi, Gulf of Khambhat etc. There are also instances of REE enrichment in the mouth of some rivers such as Mandovi and Zuari in consequence to their high heavy minerals content. Along the west coast, REE show increase with decrease in sediment size and increase in the heavy mineral fractions. The HREE content along the west coast inner shelf is very low (Fig. 4.58). The southern Kerala sector contains relatively higher HREE between 24 mg. kg^{-1} and 36 mg. kg^{-1}. Rest of the inner shelf along the west coast has recorded low HREE ranging from 12 mg. kg^{-1} to 24 mg. kg^{-1}. The HREE in general is less abundant in nature and its content in sediments is largely controlled by the mineralogy. There are a few minerals such as zircon, pyroxenes and amphiboles capable of enriched HREE presence at their formation. Since the HREE are highly immobile, diagenetic changes have least impact on their presence in minerals hosting them and thus when deposited in the near shore sector they impart higher HREE in sediments.

Comparison of REE in sediments with that of Post Archaean Australian Shale (PAAS), suggest depletion in both LREE and HREE along the Gujarat and Maharashtra inner shelf. Samples collected off Murud and Ratnagiri in Maharashtra are showing enrichment in HREE.

Off Goa and Karnataka coast, the sediments are not showing any appreciable enrichment of depletion except in the sample collected off Netravathi River mouth. LREE are showing depletion in the sediments from Sharavathi River mouth. The sediments off Kerala also show enrichment in both LREE and HREE in general. A depletion in La, Ce and Pr is found in the shelf sediments from Kasaragod. HREE is depleted in the sediments off Vizhinjam compared to PAAS.

CHAPTER 5

ROLE OF HEAVY MINERALS IN THE DISTRIBUTION OF REE

5.1 Introduction

Most of the major and trace elements are mobile during weathering and so are not reliable for petrogenetic studies of altered rocks. Since REE are highly immobile, they are used for modelling partial melting and crystal formation process (Sun and Nesbitt, 1978). During weathering or alteration of rocks there will be an interaction between the mineral phases and the fluid phase (Henderson, 1984). During the igneous crystallization, REE tend to remain in the liquid phase due to their very low partition coefficient. Clinopyroxene is one of the most important mineral in terms of removing the REE from the liquid and also selectively enriching the liquid in LREE (Henderson, 1984). Accessory minerals such as allonite, apatite, zircon and sphene, due to their high partial partition coefficient, play important roles in the distribution of REE which makes them site for the concentration of REE. In marine environment a minor amount of REE may be getting released from the minerals and enter in the sedimentary environment in solution. Bulk of these REE can be loosely held on clays and take part in exchange reactions (Roaldset and Rosenqvist, 1971). The REE concentration is low in quartz and is more in clays. The relatively high concentration of the REE in the detrital fractions of transported materials, rather than dissolved portion, suggest that the REE pass from weathering to deposition almost exclusively without taking part in any significant chemical process. The REE supplied in a dissolved state to the ocean enter a number of authegenic minerals, notably ferromanganoan-oxy-hydroxides and get deposited on the seafloor.

The enrichment of REE in nearshore sediments is controlled by factors such as the composition and mineral phases of the source rock, oxidation-reduction condition of the depositional basin, texture and composition of the sediments on the seafloor, weathering, diagenesis etc. The inner shelf sediments along the west coast of India are mostly derived from the hinterland rocks. Since weathering and diagenesis will not cause many changes in the original REE characteristic, terrigenous minerals mostly reflect the REE signature of hinterland source rocks (Sholkovitz et al. 1994, Chaudhuri and Cullers 1979). This signifies the role of hinterland rocks in governing the REE distribution in the nearshore sediments. The sandy sediments, in general, exhibit lower incidence of REE compared to the silty and clayey sediments. Study by George and Christian (2002) found lowest REE associated with sand fractions and enrichment in LREE in clay and silt fractions. Considering the electropositive nature of REE they are attracted towards the surfaces of clay minerals which are mostly electronegative. This results in the enrichment of REE in clayey sediments. Kaolinite has the ability to adsorb REE on its surface. Prudencio et al (1989) established positive correlation between the light and intermediate REE and the kaolinite content of the clay sized fractions.

Along northern Saurashtra, Maharashtra and Karnataka coast the hinterland mainly exposes Deccan trap basalts, which exhibit LREE-enriched character (Banerjee et al. 1996). On weathering, these tholeiitic basalts alter to clay minerals which get washed off and deposited in the near shore areas. The REE released during the weathering are retained in the clay minerals so produced (Price et al. 1991).

Along southern Karnataka and Kerala, the hinterland rocks are mostly of Pre-Cambrian age comprising of charnockites, peninsular gneiss, biotite gneiss, granite gneiss etc. Charnockite and charnockitic gneiss have preponderance over all other crystalline rocks covering 40-50% of the total area of the State of Kerala. The charnockites are well-exposed in the central and northern parts of Kerala including the high hills of the Western Ghats (Geological Survey of India, 2005). Charnockites being the dominant litho-type, these could be the dominant source of HM found enriched along the beaches and nearshore areas along Kerala coast.

Heavy minerals such as monazite, garnet, sphene, apatite, zircon, amphibole and pyroxene contain fairly high REE (McLennan 1989; Jung et al. 2012; Lopez et al. 2005; Hanson 1980). As a result the coastal sediments containing these minerals will be reflecting relatively higher REE content. Since HM generally constitute a major part of the sandy sediments in the beach and inner shelf environments, the higher REE observed in the inner shelf sand-dominated sediments of the west coast of India could be due to their contribution. Considering that heavy minerals are responsible for the enrichment of REE in the coastal sediments, an attempt is made in this chapter to compare the distribution of REE in the inner shelf sediments and the role of heavy minerals and other agencies operating in this regime. Since the heavy mineral data is restricted in nature, comparison of REE with heavies is made on a general basis without any contour distribution map.

5.2 Heavy minerals as source of REE

5.2.1 Gujarat andMaharashtra Inner shelf

In Gujarat, the coastal tract is covered mainly by Quaternary formations with occurrences of a few Tertiary and Trap rocks. Silt and clay are the dominant sediment types covering the inner shelf along Gujarat coast. Larger sand bodies and isolated gravel are also present in this sector. In some places the seafloor is rocky. The study of the inner shelf sediments off Gujarat by GSI has revealed low heavy mineral content. The heavy mineral content is mostly < 1 % along Saurashtra coast. Pyroxene, epidote, hornblende, biotite, chlorite, ilmenite, magnetite, zircon, tourmaline, garnet, sillimanite, rutile and monazite are the HM present in sediments. (Sukumaran et al. 1999; Zaheer et al. 2010).

In the Gulf of Khambhat, heavy minerals such as pyroxene, magnetite and rutile along with a few incidences of epidote, rutile, ilmenite, zircon and magnetite are found in negligible proportion. Sabarmati, Mahi, Narmada and Tapi are the major rivers debouching in to this area. These rivers are draining mainly through Precambrian and also through Deccan trap and Quaternary terrains. Pyroxene, hornblende and magnetite are derived from Deccan traps and associated intrusives while weathering of metamorphic rocks have resulted in the formation of epidote, garnet, sillimanite and biotite. The metamorphic minerals are evidently re-transported from the Gulf of Khambhat by the river systems draining through the Central Indian and southern Rajasthan-northern Gujarat crystalline terrains. (Sukumaran et al. 1999a & 1999b). Smectite and Montmorillonite are the major clay minerals present followed by kaolinite, plagioclase and calcite found in the Gulf of Khambhat sediments (Zaheer et al. 2001, 2004 & 2009).

In the Gulf of Kutch, the heavy mineral contents in sediments are mostly < 1 %. Sericite, biotite, ilmenite, hornblende and sillimanite are the dominant constituents of the heavy mineral assemblage. Heavy mineral suites in sands are controlled not only by provenance, but also affected by source area weathering, process of transportation and deposition and post depositional alteration (Morton, 1985). The sorting processes caused by the shelf currents, density and grain size of the heavies have determined their distribution and deposition in the area. In this area also, presence of HM can be attributed to the hinterland rocks. A major role is played by River Indus which debouches into the Arabian Sea near Kutch. The River Indus, Kutch mainland and Saurashtra peninsula have been identified as the three major sources for sediments to the Gulf of Kutch coast. The Cretaceous, Tertiary and Quaternary formations of Kutch mainland and Saurashtra peninsula are devoid of heavy minerals. River Indus travels through varied lithology including high, medium grade metamorphic, sedimentary and igneous rocks of the Himalayas and discharges copious quantity of sediments in to the Arabian Sea, (Prizomwala et.al, 2012) it can be considered as the major source for heavy minerals present in sediments. Pyroxenes, hornblende and sillimanite probably are sourced from the mafic granulites and high grade meta-sediments of the Himalayan terrain. Ilmenite, magnetite and zircon are derived from a mixed source of igneous and metasedimentary rocks of Himalayas and the Deccan Traps of the peninsula (Jayaprakash et al. 2014). The semi-enclosed Gulf of Kutch adjoining Kandla as well as the western shelf of Gujarat off Okha are dominated by clay and silt. Illite and clinochlore are the dominant clay minerals in the Gulf of Kutch (Jayaprakash et al. 2013).

The Maharashtra inner shelf is covered by silty clay and clayey silt (Rao et al. 2001&2002). This sector shows considerable variation in the heavy minerals. The shelf south of Ratnagiri contains relatively more heavies than the sector north of it. The inner shelf between Vengurla and Calangute contains moderate concentration of hornblende, sillimanite, chlorite, augite, biotite, iron-oxide and occasional grains of tourmaline, hypersthene, garnet, zircon and rutile. The hinterland of the area comprises basic and ultra-basic rocks, granites, gneisses, quartzites, phyllites and greenschists, which are the source rocks for the heavy mineral assemblage found in the offshore sediments of the area. (Charlu et al. 1999). The inner shelf between Vengurla and Mumbai contain insignificant quantity of HM such as hornblende, sillimanite, chlorite, augite, biotite, magnetite, with occasional grains zircon, rutile and hypersthene except in Mirya and Kalbadevi bays (Venkatesh et al. 1986(a) & 1986(b)). In Mirya Bay and Kalbadevi Bay, the total heavies vary between 2.5 % and about 6 %. Ilmenite and magnetite are the dominant heavy minerals with, rutile, clinopyroxine, hornblende, tourmaline, zircon, garnet, sillimanite and epidote in minor proportions (Sukumaran et al. 1990).

The inner shelf north of Ratnagiri mostly contains less than 1% heavies which decrease from Ratnagiri to Mumbai. Clinopyroxine, ilmenite, magnetite, spinel, zircon and rutile constitute the dominant heavies in this sector. The heavy mineral assemblage in the northern sector between Ratnagiri and Mumbai are characterized by first cycle sedimentary structures like fractures and sharp sages indicating proximity. Kaolinite and montmorillonite are the major constituent of clay along Maharashtra shelf and its provenance may be Deccan trap basalt (Bagchi et al. 1992; Venkatesh et al. 1993; & 1994; Abdulla et al. 2008; Kumaran et al. 2009 & 2010).

The HM along the Gujarat-Maharashtra coast show an inconsistent distribution. Some sectors such as south of Ratnagiri, between Mahim and Daman, heavies are present in relatively higher quantity compared to the rest of the shelf. The distribution pattern of REE also shows corresponding highs along these sectors whereas its content is low in the rest of the shelf. It can be observed that the dominant heavies present in most of the inner shelf sediments are pyroxenes and amphiboles which are known to contain REE. Minerals such as zircon, garnet, monazite etc, which are the principal detrital minerals carrying REE, are present in very small or negligible proportion in the sediments. Along the entire west coast, the Gujarat-Maharashtra sector has the lowest content of REE in sediments. Pyroxenes and amphiboles appear to be the major sources of REE in sediments along this sector in addition to the contribution by minerals such as monazite, garnet and zircon. Considering the presence of kaolinite in good amounts along the Maharashtra coast, the relatively higher content of REE in this sector compared to that of Gujarat could be due to the supplement of these metals by the clay minerals. The REE content is high in the Mirya Bay and Kalbadevi Bay where the heavies vary between 2.5 % and about 6 %. The low heavy mineral content all along Gujarat coast is also reflected by the low REE content in sediments.

5.2.2 Goa and Karnataka Inner shelf

The inner shelf of Goa and Karnataka is mostly covered by silty clay and clayey silt with occasional sand pockets. In the surface sediments off Goa, the heavy mineral content varies from 0.57 % to 13.85 % with magnetite (0.21% to 0.71%) and ilmenite (0.23% to 4.59%) as dominant minerals. Medium to fine sand is the dominant sediment along the Goa beach. Other heavy minerals in varying amounts are rutile, orthopyroxene, garnet, biotite, staurolite, chlorite, glauconite, tourmaline, zircon and pyrite. Amphiboles and clino-pyroxene are also present in considerable amounts in the sediments (Sukumaran et al. 1997). The above data suggest a moderately high heavy mineral content along the entire coast of Goa. The REE distribution map off Goa coast also shows a consistent presence of REE in moderate proportion along the entire coastal stretch pointing to their complimenting nature.

The uplands of Goa are formed of a variety of rock types which include phyllites, quartzites, greywackes, amphibolites, pyroxenites, granites and gneisses, micaceous quartzites and basic intrusives of Precambrian age and

Deccan trap basaltic flows. Most of the HM present in the offshore sediments have appropriate source rocks in the hinterland of Goa. Epidote/zoisite and chlorite reflect low grade greenschists as the source, while staurolite, hornblende and garnet are from higher grade metamorphic rocks. Rutile and tourmaline could come from the granites and gneisses or even pegmatite veins traversing the gneisses. Recycled sources could supply the well-rounded tourmaline and zircon. The pyroxenes could come from basaltic rocks, but coarse nature of most of the grains suggests basic plutonic rocks as the source. Majority of the grains are angular suggesting only short transport.

In Karnataka along Mangalore-Coondapur sector, the heavy mineral content varies from 0.28 % to 2.23 % (Charlu el al. 2000). Important rivers debouching into the Arabian Sea in this sector are Nethravathi, Kali, Sharavathi, Zuari and Mandovi. These rivers are flowing through rock formations like the greenschists of north Karnataka and Goa and the granite-gneisses of south Karnataka. Varied types of basic and ultrabasic rocks also occur in the adjoining terrains.

The heavy mineral content between Bhatkal and Karwar range from 0.12 % to 2.1 % in the surface sediments (Nambiar et al. 1990 (a); Charlu et al. 1995 and Chandra et al. 2001). Ilmenite and epidote are the predominant heavy minerals in the offshore sediments while magnetite, orthopyroxene, hornblende, rutile, tourmaline, staurolite, monazite, apatite, garnet, sillimanite and zircon occur in low quantities. The heavy mineral grains are angular in shape indicating low textural maturity and a nearby source for them. The hinterland consisting of greenschists, granite gneiss, basic and ultrabasic rocks are the source rocks for these HM in the offshore samples (Nambiar et al. 1990 (b)). Heavy minerals such as monazite, garnet, sphene, apatite, zircon, amphibole and pyroxene contain fairly high REE (McLennan 1989; Jung et al. 2012; Lopez et al. 2005; Hanson 1980). Considering the presence of these heavy minerals in low to moderate amount in inner shelf sediments of this sector, and the positive correlation shown with REE content, it will be appropriate to suggest their mutually complimenting association. Along this sector too, kaolin and other clay minerals such as illite and montmorillonite are reported to occur in dominant quantities. So it could be logical to expect a part of the REE to be the contribution of these minerals to the total REE associated with sediments in the inner shelf.

Presence of authigenic pyrite as spherical nodules and coating on shell fragments is a significant find in some segments along Karnataka-Goa sector. Such sediments are fairly abundant in organic matter also. Oxygen deficient anoxic bottom environments are known to favour precipitation of authigenic sulphides. On the otherhand precipitation of REE in sea water is favoured in an oxygenated environment. This also could be one of the factors responsible for the reduced incidence of REE in this sector.

5.2.3 Kerala Inner shelf

The inner shelf between Ponnani and Kochi contains an average of 3.5 % of HM which include pyroxene, amphibole, as major constituents and zircon and garnet as minor minerals (Nair et al. 1986). These minerals are known to contain REE. The Ponnani-Kochi sector, in general, contains about 4 % of heavies in the inner shelf area. The average concentration of heavies off Alappuzha and Quilon is about 4.5 % and consist of ilmenite, leucoxene, zircon, rutile, magnetite, sillimanite, monazite and ferromagnesian minerals. These heavy minerals occur more abundantly in finer fractions (+120 and -120) (Senthiappan et al. 1985; 1989(a)). The average HM off Attipara-Anjengo sector is about 3 %. Seabed samples from Chavara and Varkala contain an average of 5 % of heavy minerals in the inner shelf sector whereas Quilon sector contains about 4.5 % of heavies (Senthiappan et al. 1989(b)). The average concentration of HM in the samples analysed between Muttam and Vizhinjam is about 5 % (Nambiar et al. 1994). Generally, it is not possible to relate the heavy mineral suites of the beach and shelf sediments to only one source rock. The suites of modern beach and shelf sands are the result of complicated processes by which the original composition of the fluviatile sediments is largely obliterated. Unstable minerals are chemically or mechanically destroyed or fractured and the stable minerals are sorted corresponding to grain size, shape and density. A distinct heavy mineral association marked by predominance of ilmenite, sillimanite and garnet and by the presence of appreciable quantities of zircon, monazite and kyanite and less frequently of pyroxenes, staurolite, spinel etc. characterise the sediments of the area. This heavy mineral assemblage is suggestive of its origin from a mixed metamorphic and igneous terrain with a predominant contribution from metamorphic rocks. Reworking of older sediments may also supply a part of the heavy minerals. The red "Teri" sands of the area contain an average of 3.5% heavy minerals, whereas the Mio-Pliocene Varkala sediments have less than 1% heavy minerals. It is possible that a part of the HM in beach and shelf sediment might be derived from reworking of "Teri" sand (Nambiar et al. 1990).

The heavy mineral content in sediments along the northern Kerala between Ponnani and Kasaragod coast is found to be very low and varies between <1 % to 2 % (Sukumaran et al. 2002; Jayakumar et al. 2006; 2007; Kannan et al. 2010). The inner shelf along this sector is covered by silty clay and clayey silt. The lesser abundance of heavies in this sector could be due to the dominance of muddy sediments containing very small quantity of heavy minerals.

A comparative study of REE and heavy mineral content in sediments along Kerala coast suggests a direct correlation between these two. The southern Kerala sector has an average heavy mineral content of about 4.5 % whereas in the northern sector its content is about 1 %. Correspondingly the REE content is also found to be more along the southern sector compared to the northern sector.

5.3 Conclusion

The seafloor within the inner shelf off Kerala is dominated by sand in the southern part and by terrigenous silty clay and clayey silt along the northern sector. The southern shelf holds considerable concentration of monazite, garnet, sphene, apatite, zircon, amphibole and pyroxene. REE content along this sector is between 185.11 mg.kg^{-1} and 319.66 mg.kg^{-1}. These heavy minerals are known to contain high REE and this could have resulted in the enrichment of the rare metals in this sector. Along northern sector the REE content ranges between 9.15 mg.kg^{-1} and 199.56 mg.kg^{-1}. The heavy mineral content in sediments along the northern Kerala between Ponnani and Kasaragod coast is found to be very low and varies between <1 % to 2 %. The low content of zircon and garnet along this sector which are the main detrital minerals contributing HREE, could be the reason for the low HREE observed all along the shelf of Kerala coast.

REE contents of the surface sediment along Karnataka and Goa inner shelf vary between 36.44 mg. kg^{-1} and 174.6 mg. kg^{-1}. The Honnavar and Karwar segment along this sector show the lowest concentration of REE. The inner shelf between Bhatkal and Mangalore in the south and Karwar and Panaji in the north show moderate REE content. The inner shelf of Karnataka and Goa is mostly covered by silty clay and clayey silt with occasional sand pockets. Between Mangalore and Karwar, the heavy mineral content varies from 0.28 % to 2.23 % in the inner shelf sediments. The heavies along this sector are mostly derived from greenschists, granite gneiss, basic and ultrabasic rocks outcropping in the hinterland. Along this sector kaolin, illite and montmorillonite are the important clay minerals present in the inner shelf. The clay minerals also might have contributed a part of REE associated with sediments in the inner shelf. In the inner shelf off Goa, the average heavy mineral content is about 5% and this sector shows a consistent REE content too. The comparison of heavy and REE distribution along Karnataka and Goa inner shelf suggest their complementing nature.

Maharashtra-Gujarat sector has recorded the lowest content of REE in sediments along the entire west coast. Silt and clay are the dominant sediment and along Maharashtra and Gujarat inner shelf with smectite and montmorillonite as the main components. In inner shelf south of Ratnagiri, and between Mahim and Daman, heavy mineral content is high compared to rest of the shelf. The REE is also showing higher abundance along these sectors whereas its content is low in the rest of the shelf suggesting their interdependence. Considering the presence of kaolinite in good amounts along the Maharashtra coast, the relatively higher content of REE found in this sector compared to that of Gujarat could be due to the enrichment of these metals by the clay minerals.

The above discussion points towards a close and direct link between the heavy mineral content of the sediments and their REE concentration. Based on this, it is suggested that along the west coast of India, the REE content of sediments in the inner shelf is mostly due to the HM present in them. In addition to this, mineralogy and texture of the shelf sediments also appear to have a significant role in the distribution of REE. Along the west coast, the sandy sediments present along the Kerala coast are found to contain maximum REE compared to rest of the west coast due to their high heavy mineral content. In the inner shelf of Gujarat, the heavy mineral content is extremely low, even then the REE content is found to be moderate (106.53 mg. kg^{-1} to 154.48 mg. kg^{-1}). This suggests the role of clay minerals in concentrating REE in fine sediments apart from the contribution by detrital minerals such as pyroxenes and amphiboles present. It could be concluded that apart from heavies, REE are also contributed by clay and silt, along the west coast. A drop in the REE content in sediments along the river mouths could be due to its dilution by the influx of sediments from provenances depleted in REE.

In addition, the texture and composition of the shelf sediments also have significant role in the distribution of REE. It is an established fact that the REE can get adsorbed on to the surfaces of fine clay and silt particles making them sources of these metals. The ion adsorption clays of China are one of the prime sources of REE in the world. Kaolin is known to adsorb REE on their surfaces. Likewise, along Maharashtra too REE distribution is very consistent between 111.78 mg. kg^{-1} and 131.02 mg. kg^{-1} despite the inconsistency shown in heavy mineral content in sediments. This could be due to the presence of pyroxenes derived from Deccan trap basalt, acting as source of REE, in the finer sediments and also due to the adsorption of these metals on the clay surfaces due to their opposite polarity. In general, it could be concluded that, apart from REE contribution by heavies, clay and silt also play a noteworthy role in the enrichment of these metals in sediments.

A drop in the REE content in sediments along the mouths of some of the major rivers was observed at several places along the west coast of India. The rivers while debouching into the sea offload huge quantity of sediments brought from the hinterland. If the provenance rocks are depleted in REE, then that signature will be reflected by the shelf sediments. So it should be important to understand the geochemistry of the upstream rocks in areas where major rivers are debouching into the sea. The dilution by river sediments appear to be a major reason for the low content of REE exhibited by shelf sediments along the mouths of Bharatapuzha, Nethravathi and Sharavathi river mouths and also in the Gulf of Khambhat and Gulf o f Kutch where several rivers are debouching.

CHAPTER 6
SUMMARY AND CONCLUSION

The west coast is characterised by a spindle shaped continental shelf with maximum width off Maharashtra which narrows both towards Gujarat in the NW and Kerala in the SE. The inner shelf along west coast is mostly restricted to 50 m water depth. The bathymetric contours run almost parallel to the coast indicating the absence of any topographical irregularities except off Goa, Karwar, Malpe and Mt.Dilli. The seafloor gradient is less in the northern parts where the shelf width is more.

West Coast inner shelf is drained by a number of prominent river systems flowing through geologically interesting hinterland rock formations of different ages. Sea level fluctuations, tectonism and global glaciation had left a strong imprint in the depositional history. The inner shelf is mostly covered with sediments of Pleistocene to Recent Age, with the coarser sediments occupying the near shore areas and the fines in deeper parts of inner shelf.

The Gujarat inner shelf is covered mostly by silty clay and clayey silt. Along sectors such as Mandovi and Dwarka, the seafloor is rocky and is devoid of sediments. Sand is present within the Gulf of Kutch, southeast of Porbandar and also in the Gulf of Khambhat. The Gulf of Khambhat is covered by very fine sand, silt and clay. Fine sediments are strongly fine skewed to coarse skewed near the coast and confluences of rivers suggesting mixing of the relatively coarser material with fine sediments. Coarse fractions contain HM such as ilmenite, garnet, rutile, biotite, glaucony, amphibole and epidote in small quantities. The sandy sediments are better sorted than the finer silty and clayey sediments. The sediments near to the coast and river mouths are strongly fine skewed to coarse skewed suggesting mixing of coarser and finer sediments.

The metamorphosed and associated intrusive of Pre-Cambrians along with sedimentary rocks of Mesozoic and Cenozoic age and Deccan volcanic of Cretaceous to Eocene age are the lithologies exposed along the coastal tract of

Gujarat. Miliolitic limestone exposes almost all along the length of the Saurashtra coast.

The Maharashtra coast is quite straight and the hinterland exposes mostly Deccan trap basalt. In some of the coastal belt areas rocky exposures with steep cliffs are also seen. Deposition of large quantity of sediments has caused flattening of the seabed near the major river mouths. Maharashtra inner shelf is covered with silty clay and clayey silt reflecting the finegrained nature of the hinterland rocks. The sediments are very poorly sorted suggesting variable energy condition during deposition.

Along Karnataka, the continental shelf has maximum width off Karwar and a minimum width off Mangalore. The coastal part of Goa and Karnataka states is occupied by Gneissic Complex consisting of granites and gneisses of different ages. Silty clay and clayey silt cover most of the inner shelf off Goa and Karnataka. Altered potash and plagioclase feldspars are the abundant constituents after quartz, followed by HM like ilmenite, sillimanite, magnetite and garnet with minor amount of pyroxene.

The entire inner shelf south of Quilon and the deeper part of the inner shelf between Ponnani and Quilon along Kerala is covered by sand. North of Quilon upto Kasaragod, the shallow part of the seafloor is almost entirely covered by silty clay and clayey silt. The deeper part of the inner shelf between Kasaragod and Ponnani is covered with muddy sediments. Quartz and plagioclase feldspar are the essential constituents of sandy sediments whereas magnetite, garnet, zircon, sillimanite, hypersthene, hornblende and clino-pyroxene constitute the minor minerals.

The sediment distribution along the inner shelf off west coast emphasizes the role of hinterland geology, climate and littoral and shallow water currents active in the area. The Kerala coast is dominated by sandy sediments south of Quilon and also along the outer part of inner shelf off Ponnani to Cape Comorin. Rest of the seafloor is covered with muddy sediments. Along Karnataka, Goa and Maharashtra coast silt and clay cover the seafloor of the inner shelf with pockets of sand. Even though silt and clay are the main sediment type covering the inner shelf along Gujarat coast, larger sand bodies and isolated gravel are also present in this sector.

REE in the inner shelf sediments ranges from 9.15 mg. kg^{-1} to 319.66 mg. kg^{-1}. Along Maharashtra and Gujarat coast REE vary between 106.53 mg. kg^{-1} and 154.48 mg. kg^{-1}, LREE between 89.34 mg. kg^{-1} and 137.72 mg. kg^{-1} and HREE between 14.95 mg. kg^{-1} and 20.43. High LREE content is recorded in the area off Jakhau and south of Devgarh whereas between Surat and Malwan HREE is high. Gulf of Khambhat and Gulf of Kutch sediments have low content of both LREE and HREE.

Gujarat-Maharashtra sector has recorded the lowest content of REE in sediments along the entire west coast. REE content is relatively high between Malvan and Devgarh, Mahim and Daman and between Dwarka and Jakhau where as it is very low in Gulf of Khambhat and Gulf of Kutch. The low REE content in the Gulf of Khambhat could be due to dilution by the sediment flux from the rivers debouching into the Gulf of Khambhat as well as the low REE signature of the source rocks. The tidal currents causing sediment mixing also could obliterate the original REE characteristics of the sediments.

Along Saurashtra coast, the heavy mineral content is mostly <1 %. Pyroxene, amphiboles, zircon, garnet and monazite are the heavy minerals that appear to have contributed REE to sediments. The pyroxenes and amphibole content is quite high compared to rest of the heavies and these two minerals appear to have contributed bulk of the REE along this sector. The low REE off Gulf of Khambhat could be due to the dilution by the fluviatile sediments deposited by several rivers joining the Gulf here. Clay minerals such as smectite and montmorillonite, followed by kaolinite also would have contributed REE present in sediments.

The Maharashtra inner shelf is covered by muddy sediments and this sector has recorded the lowest content of REE in inner shelf. The coastal stretch between Mahim and Daman contain maximum heavies along Maharashtra-Gujarat. Minerals such as amphiboles, pyroxenes, garnet, zircon and rutile are the major contributors of REE. The basic and ultra-basic rocks, granites and gneisses are the source rocks for the HM in the offshore sediments along Maharashtra. In Mirya Bay and Kalbadevi Bay, the average heavy mineral content is 4.25 % and REE content is also high along this sector. The inner shelf north of Ratnagiri mostly contains less than 1% heavies which progressively decrease from Ratnagiri to Mumbai and in this sector the REE content is also low.

Geologically Goa constitutes the northwesterly extension of the granitoid-greenstone terrain of Karnataka, comprising rocks of Precambrian age. Deccan Trap is exposed on the NE border of Goa. The Goa coast is also covered with muddy sediments with small lenticular sand bodies. The REE content in this sector is very consistent with average content of 140 mg. kg^{-1}. ΣREE of samples collected from Mandovi estuary showed significant correlation with clay and silt fractions and its content in sediments is primarily controlled by its texture. Consistent REE patterns of sediments from Zuari estuary and adjacent continental shelf may be reflecting the composition of the dominant detrital minerals delivered to the estuary/shelf. In the surface sediments off Goa, the heavy mineral content varies from 0.57 % to 13.85 % with heavy minerals such as pyroxene, garnet, zircon and amphiboles. The REE distribution off Goa coast also shows consistency with the distribution of heavies pointing to their complimenting nature.

REE content of the surface sediment along Goa and Karnataka inner shelf vary between 36.44 mg. kg^{-1} and 174.6 mg. kg^{-1} and is relatively low compared to Kerala sector. LREE vary between 20.54 mg. kg^{-1} and 155.05 mg. kg^{-1} and the highest content is observed between Karwar and Panaji and also north of Mangalore. The Malpe- Bhatkal sector shows moderate LREE content. Lowest LREE is recorded off Honnavar and south of Mangalore. Goa inner shelf shows a consistent concentration LREE concentration of 140 mg. kg^{-1} to 160 mg. kg^{-1}.

From Karwar to Bhatkal there is a gradual decrease in LREE from 120 mg. kg^{-1} to 20 mg. kg^{-1}. The lowest concentration is in the shelf off the mouth of Sharavathi River. LREE shows a concentration of 120 mg. kg^{-1} to 130 mg. kg^{-1} off Coondapur which further increases 160 mg. kg^{-1} towards Mangalore. There is a gradual drop REE content in the deeper parts of the inner shelf. HREE content is too low along Karnataka and Goa sector with a lowest content of 11.96 mg. kg^{-1}

and highest content of 19.72 mg. kg^{-1}. There is a steep drop in the HREE content off Sharavathi and Nethravathi River mouths.

The inner shelf of Goa and Karnataka is mostly covered by silty clay and clayey silt with occasional sand pockets. Along Karnataka inner shelf, the heavy mineral content is relatively low. Mangalore-Coondapur sector, the average heavy mineral content is 1.3 %. The average heavy mineral content between Bhatkal and Karwar is 1.1 % in the surface sediments. The heavy mineral assemblage found in this sector contains pyroxene, amphibole, monazite, garnet, sphene and zircon which are known carriers of REE. The distribution of heavy minerals all along the west coast is showing a decline from shallow to deep water. REE are also showing identical distribution pattern. The low to moderate content of HM in the inner shelf and the positive correlation shown with REE suggest their compatible association. Kaolin, illite and montmorillonite also would have contributed a part of REE associated with sediments in the inner shelf.

Presence of authigenic pyrite along Goa-Karnataka sector suggests the presence of reducing depositional environment. Since precipitation of REE in sea water is favoured in an oxygenated environment, the relatively low content of REE in some sectors could be the result of an anoxic environment.

The inner shelf sediments between Ponnani and Vizhinjam show >200 mg. kg^{-1} REE which is the highest recorded along the west coast. Moderate to low REE is observed in the northern sector between Ponnani and Kasaragod. LREE in surface sediments within the Territorial Waters off Kerala ranges between 5.61 mg. kg^{-1} and 306.31 mg. kg^{-1}. Its content is highest in sediments south of Ponnani to Vizhinjam and moderate to low LREE north of Ponnani. The REE content is gradually decreasing from land to offshore. HREE content in the sediments is very low along entire Kerala coast and ranges from 2.91 mg. kg^{-1} to 36.8 mg. kg^{-1}. The sector between Calicut and Quilon show relatively higher content whereas Kanhangad and Someshwara, south of Quilon and off Ponnani show very low HREE in sediments. The inner shelf between Ponnani and Kochi contains an average of 3.5 % of HM which include pyroxene, amphibole, as major constituents and zircon and garnet as minor minerals (Nair et al. 1986). The average concentration of heavies off Alappuzha and Quilon is about 4.5 % and consist of ilmenite, leucoxene, zircon, rutile, magnetite, sillimanite, monazite and ferromagnesian minerals. The heavy mineral content in sediments along the northern Kerala between Ponnani and Kasaragod coast is found to be about 1 %. The inner shelf along this sector is covered by silty clay and clayey silt. The lesser abundance of heavies in this sector could be due to the dominance of muddy sediments containing very small quantity of heavy minerals.

Relating REE with that of heavy minerals in sediments, it is found that the incidences of REE are more in sectors where abundance of HM is reported. Even though several prominent perennial rivers are debouching into Arabian Sea along Kerala coast, there is no marked drop in REE along most of these river mouths. This possibly suggests high REE signature of the rocks exposed in the drainage basins of these rivers. The heavy minerals derived from the hinterland rocks appear to be the major source of REE along west coast of India.

A positive correlation is observed between the REE and heavy concentration along the west coast. The southern Kerala inner shelf has recorded the highest concentration of HM along the entire west coast and it is in this sector the highest incidence of REE is observed. Along the northern Kerala sector between Ponnani and Kasaragod, the heavy mineral content of the sediments is low to moderate and REE distribution pattern also follows a comparable lower trend.

Monazite is a known source of LREE and this mineral might have contributed bulk of the LREE present in sediments. Minerals such as apatite and sphene too have significant presence in the southern inner shelf of Kerala. These minerals also contain LREE and would have acted as the source of these metals. HREE is mostly derived from minerals such as zircon, garnet, pyroxenes and amphiboles whose concentration is relatively low in the inner shelf sediments along west coast. These minerals are present in low to moderate quantities along the southern Kerala sector causing a relatively high abundance of HREE along this sector compared to rest of the west coast inner shelf. Pyroxenes and amphiboles are the main source of HREE in the inner shelf sediments off Gujarat.

Considering the vastness of the area studied, the sampling density is inadequate to comprehend small changes in the REE distribution. Moreover, a large number of rivers are debouching into the Arabian Sea and to evaluate their role in controlling REE distribution in shelf sediments, samples need to be collected from upstream at regular intervals from each of these rivers. Collecting core samples from inner shelf at regular intervals and evaluating the REE content will help in understanding their spacial and temporal distribution.

Based on REE content in surface sediment, the entire west coast inner shelf is classified into four main sectors.

1. The high REE Sector along southern Kerala coast between Ponnani and Vizhinjam.
2. The moderately high sector between Ponnani in Kerala to Ratnagiri in Maharashtra and between north of Porbandar to Jakhau in Gujarat.
3. Low concentration sector between Ratnagiri in Maharashtra to Porbandar in Gujarat.
4. Very low concentration sector in the Gulf of Khambhat, Gujarat.

The study also suggests heavy minerals as the central factor controlling the distribution of REE in the inner shelf sediments along the west coast of India. Clayey sediments containing kaolinite appear to have augmented the REE content in some sectors due to their adsorption.

Recommendations

Highest concentration of REE within the inner shelf sediments is found off southern Kerala coast between Alleppey and Vizhinjam, which is contributed by heavy minerals. Since the present study is restricted to surface sediments, a detailed exploration programme can be mounted for evaluating the spacial and temporal distribution of REE in the inner shef sediments between Quilon and Vizhinjam by collecting core samples.

Table 2.1 The sample locations, sediment type and the REE content (mg. kg^{-1}) in surface sediments.

Samp. Nos	Lat. (Deg)	Long. (Deg)	Water depth (m)	Sedi. Type	La	Ce	Pr	Nd	Eu	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣLREE	ΣHREE	ΣREE
G-1	22.64	69.01	59.7	Clay	35.15	64.04	7.73	24.65	1.03	5.12	5.29	0.78	4.22	0.80	2.31	0.50	2.36	0.50	137.72	16.76	154.48
G-2	22.56	69.86	40.1	Clay	27.61	51.17	6.30	19.18	0.85	4.24	4.60	0.69	3.82	0.72	2.07	0.50	2.05	0.50	109.35	14.95	124.3
G-3	21.59	69.57	22.0	Clay	25.73	47.57	5.94	19.38	0.80	3.93	4.50	0.69	3.88	0.74	2.13	0.50	2.10	0.50	103.35	15.04	118.39
G-4	21.49	69.52	34.5	Clay	27.60	51.29	6.54	20.61	0.92	4.38	5.02	0.78	4.51	0.83	2.37	0.50	2.30	0.50	111.34	16.81	128.15
G-5	21.02	72.65	17.9	Clay	22.25	41.29	5.51	15.47	0.86	3.96	4.92	0.77	4.76	0.90	2.53	0.50	2.31	0.50	89.34	17.19	106.53
G-6	20.88	72.56	31.0	Clay	29.69	55.21	7.03	19.51	1.07	5.13	5.94	0.93	5.41	1.02	2.85	0.50	2.69	0.50	117.64	19.84	137.48
G-7	20.81	70.50	19.5	Clay	27.12	50.56	6.23	18.48	0.92	4.4	4.98	0.77	4.49	0.83	2.33	0.50	2.25	0.50	107.71	16.65	124.36
G-8	20.65	70.38	41.0	Clay	30.83	56.50	7.05	20.24	1.03	4.94	5.68	0.84	5.02	0.93	2.56	0.50	2.48	0.50	120.59	18.51	139.10
G-9	17.78	72.87	25.5	Clay	26.38	49.51	6.28	18.29	0.98	4.53	5.51	0.84	4.97	0.93	2.55	0.50	2.35	0.50	105.97	18.15	124.12
G-10	17.78	73.07	9.9	Clay	22.98	43.73	5.66	16.60	0.90	4.08	5.17	0.82	4.96	0.92	2.55	0.50	2.41	0.50	93.95	17.83	111.78
G-11	16.98	73.23	18.3	Clay	27.07	52.04	6.5	19.24	1.08	4.66	6.05	0.94	5.76	1.06	2.89	0.50	2.73	0.50	110.59	20.43	131.02
G-12	16.98	73.09	38.9	Clay	24.76	47.18	5.91	17.95	0.90	4.20	5.23	0.80	4.72	0.87	2.44	0.50	2.29	0.50	100.90	17.35	118.25
G-13	14.83	74.08	10.6	Silty clay	33.75	63.91	7.50	22.31	1.07	5.13	5.73	0.83	4.87	0.93	2.61	0.50	2.59	0.50	133.67	18.56	152.23
G-14	14.74	73.94	36.0	Silty clay	31.78	60.81	7.04	21.44	0.99	4.90	5.44	0.79	4.65	0.89	2.47	0.50	2.49	0.50	126.96	17.73	144.69
G-15	14.28	74.40	2.8	Clay	3.32	6.04	1.41	6.97	0.64	2.16	3.14	0.6	4.22	0.87	2.75	0.48	3.31	0.53	20.54	15.90	36.44
G-16	14.19	74.37	3.1	Clay	7.89	18.70	2.61	12.16	0.90	3.01	4.30	0.72	5.01	1.05	3.21	0.49	3.19	0.53	45.27	18.50	63.77
G-17	13.95	74.32	38.9	Clay	28.83	53.19	6.42	19.53	0.92	4.98	5.57	0.78	4.31	0.82	2.35	0.50	2.35	0.50	113.87	17.18	131.05
G-18	13.95	74.44	20.8	Silty clay	30.03	56.11	6.59	19.86	0.93	5.04	5.71	0.81	4.65	0.92	2.67	0.50	2.72	0.50	118.56	18.48	137.04
G-19	12.85	74.81	9.0	Clay	37.72	75.82	8.13	26.01	1.14	6.23	6.62	0.88	4.88	0.92	2.66	0.50	2.59	0.50	155.05	19.55	174.60
G-20	12.83	74.73	8.0	Clay	22.52	51.80	4.97	18.72	0.98	3.75	3.86	0.60	3.42	0.64	1.70	0.30	1.67	0.28	102.74	12.47	115.21
G-21	12.81	74.81	6.0	Silty clay	28.52	50.23	5.69	20.52	1.08	3.78	3.88	0.58	3.24	0.57	1.63	0.23	1.57	0.26	109.82	11.96	121.78
G-22	12.78	74.72	28.0	Silty clay	32.26	61.27	7.01	21.1	0.98	5.38	6.11	0.86	4.97	0.98	2.88	0.50	2.92	0.50	128.00	19.72	147.72
G-23	12.47	74.99	6.0	Clay	21.35	40.62	6.90	34.11	2.97	8.59	11.90	1.81	10.00	1.96	5.25	0.79	4.41	0.66	114.54	36.80	151.34

Samp. Nos	Lat. (Deg)	Long. (Deg)	Water depth (m)	Sedi. Type	La	Ce	Pr	Nd	Eu	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣLREE	ΣHREE	ΣREE
G-24	12.47	74.97	8.0	Clay	35.53	70.26	7.76	24.98	1.09	5.87	6.57	0.89	4.93	0.93	2.67	0.50	2.68	0.50	145.49	19.67	165.16
G-25	12.42	74.87	9.0	Clay	9.21	27.00	2.10	7.53	0.44	1.62	1.56	0.28	1.65	0.32	1.08	0.20	1.28	0.21	47.90	6.58	54.48
G-26	12.40	74.82	42.0	Clay	32.14	61.54	7.18	21.71	0.99	5.43	6.07	0.83	4.70	0.90	2.59	0.50	2.61	0.50	128.99	18.70	147.69
G-27	12.21	75.11	11.0	Clay	1.08	2.16	0.43	1.56	0.06	0.32	0.58	0.09	0.79	0.18	0.68	0.13	0.93	0.16	5.61	3.54	9.15
G-28	12.16	74.99	8.0	Clay	38.80	70.25	6.84	23.45	0.47	3.84	3.15	0.45	2.08	0.37	1.11	0.19	1.21	0.20	143.65	8.76	152.41
G-29	11.93	75.29	8.0	Clay	34.74	66.90	7.53	24.88	1.06	5.62	6.21	0.86	4.80	0.92	2.69	0.50	2.75	0.50	140.73	19.23	159.96
G-30	11.86	75.12	37.5	Clay	32.87	62.13	7.18	22.07	1.06	5.49	6.16	0.85	4.75	0.90	2.58	0.50	2.56	0.50	130.8	18.80	149.60
G-31	11.24	75.46	7.0	Clay	33.25	63.97	7.48	22.55	1.05	5.51	6.25	0.85	4.71	0.91	2.57	0.50	2.58	0.50	133.81	18.87	152.68
G-32	11.18	75.63	31.5	Clay	31.89	59.94	6.98	21.09	0.93	5.16	5.45	0.71	3.96	0.76	2.23	0.50	2.34	0.50	125.99	16.45	142.44
G-33	10.68	75.89	9.8	Clay	53.87	102.10	11.50	39.73	1.54	8.32	8.03	1.00	5.15	0.95	2.67	0.50	2.61	0.50	217.04	21.41	238.45
G-34	10.63	75.78	31.4	Clay	21.77	40.01	4.02	13.89	0.50	2.63	2.01	0.50	0.77	0.50	0.50	0.50	0.50	0.50	82.82	5.78	88.60
G-35	10.18	76.11	13.5	Clay	49.3	91.86	10.7	37.84	1.44	7.76	7.69	1.00	5.17	0.96	2.68	0.50	2.60	0.50	198.90	21.10	220.00
G-36	10.1529	75.9995	29.5	Clay	44.6	82.86	9.58	35.30	1.26	6.88	6.86	0.88	4.60	0.87	2.46	0.50	2.41	0.50	180.48	19.08	199.56
G-37	9.52	76.25	15.0	Clay	49.7	93.51	10.90	37.3	1.44	7.60	7.63	0.98	5.20	0.97	2.72	0.50	2.65	0.50	200.48	21.15	221.63
G-38	9.45	76.14	37.0	Clay	42.32	78.54	9.20	32.01	1.21	6.54	6.61	0.84	4.41	0.84	2.33	0.50	2.34	0.50	169.82	18.37	188.19
G-39	9.26	76.36	13.0	Clay	78.57	143.20	15.6	55.68	1.63	10.3	7.46	0.70	2.58	0.50	1.18	0.50	1.27	0.50	304.97	14.69	319.66
G-40	9.09	76.32	33.0	Clay	43.07	79.97	9.10	30.07	1.09	6.23	5.73	0.70	3.61	0.68	1.93	0.50	1.93	0.50	169.53	15.58	185.11
G-41	8.39	76.93	38.0	Sandy clay	59.04	106.60	12.70	43.72	1.48	8.88	6.45	0.61	2.26	0.50	1.01	0.50	1.11	0.50	232.39	12.94	245.33
G-42	8.08	77.82	23.0	Silty clay	19.98	37.03	4.44	14.06	0.50	3.08	2.94	0.50	1.78	0.50	0.96	0.50	0.88	0.50	79.09	8.56	87.65

Table 3.1: Grain size, statistical and other parameters of surface sediment samples.

Samp. No	Location	Lat. (Deg).	Long. (Deg).	Water depth (m)	Median	Mean	STD	Skewness	Kurtosis	Granule	Sand %	Silt %	Clay %	Sedi. Type
G-1	Okha	22.64	69.01	59.70	9.00	8.58	1.89	-0.30	0.85	0.00	0.80	38.07	61.13	Clay
G-2	Okha	22.56	69.86	40.10	9.13	8.74	1.73	-0.24	0.86	0.00	0.55	39.24	60.21	Clay
G-3	Porbandar	21.59	69.57	22.00	9.27	9.54	2.59	0.11	0.76	0.00	2.16	36.11	61.73	Clay
G-4	Porbandar	21.49	69.52	34.50	9.03	8.57	2.24	0.14	0.69	0.00	1.95	29.78	70.22	Clay
G-5	Dandi	21.02	72.65	17.90	9.80	9.50	2.99	-0.14	0.74	0.00	0.31	35.25	64.44	Clay
G-6	Dandi	20.88	72.56	31.00	8.93	9.00	3.00	0.04	0.71	0.00	0.23	39.98	59.79	Clay
G-7	Baroda	20.81	70.50	19.50	10.11	10.05	2.53	-0.06	0.80	0.00	0.15	23.37	76.47	Clay
G-8	Baroda	20.65	70.38	41.00	9.57	9.55	2.75	-0.01	0.73	0.00	0.16	33.59	59.66	Clay
G-9	Murud	17.78	72.87	25.50	10.17	10.11	2.54	-0.08	0.83	0.00	0.37	22.27	77.36	Clay
G-10	Murud	17.78	73.07	9.90	10.47	10.32	2.58	-0.16	0.93	0.00	0.92	19.25	80.75	Clay
G-11	Ratnagiri	16.98	73.23	18.30	8.70	8.93	2.97	0.08	0.78	0.00	0.82	40.30	58.90	Clay
G-12	Ratnagiri	16.98	73.09	38.90	9.74	9.44	2.91	-0.10	0.76	0.00	1.11	28.80	70.10	Clay
G-13	Karwar	14.83	74.08	10.60	8.30	8.68	3.01	0.16	0.74	0.00	3.91	43.45	52.94	Sily clay
G-14	Karwar	14.74	73.94	36.00	8.17	8.58	3.05	0.19	0.66	0.00	1.43	47.62	50.95	Silty Clay
G-17	Bhatkal	13.95	74.32	38.90	9.43	9.29	2.97	-0.06	0.69	0.00	0.62	34.89	64.49	Clay
G-18	Bhatkal	13.95	74.44	20.80	9.28	9.26	2.93	-0.01	0.72	0.00	1.48	36.59	61.93	Silty Clay
G-19	Mangalore	12.85	74.81	9.00	9.29	9.26	2.93	-0.01	0.72	0.00	1.48	36.59	61.93	Clay
G-22	Mangalore	12.78	74.72	28.00	8.88	8.83	3.17	-0.01	0.68	0.00	2.37	41.51	56.11	Silty Clay
G-24	Kasaragod	12.47	74.97	8.00	9.26	9.34	2.91	0.00	0.83	0.00	1.59	32.71	65.70	Clay
G-26	Kasaragod	12.40	74.82	42.00	9.60	9.51	2.84	-0.05	0.76	0.00	0.84	32.45	66.71	Clay

Samp. No	Location	Lat. (Deg).	Long. (Deg).	Water depth (m)	Median	Mean	STD	Skewness	Kurtosis	Granule	Sand %	Silt %	Clay %	Sedi. Type
G-29	Cannanore	11.93	75.29	8.00	8.91	8.77	3.26	-0.04	0.77	0.00	3.59	38.11	58.30	Silty Clay
G-30	Cannanore	11.86	75.12	37.50	8.27	8.52	3.19	0.10	0.73	0.00	5.09	42.49	52.42	Silty Clay
G-31	Calicut	11.24	75.46	7.00	9.72	9.55	2.89	-0.10	0.76	0.00	1.55	30.75	67.70	Clay
G-32	Calicut	11.18	75.63	31.50	9.86	9.75	2.71	-0.07	0.75	0.00	0.35	30.30	69.35	Clay
G-33	Azhikodu	10.77	76.02	29.50	9.32	8.87	2.03	-0.38	0.78	0.00	1.84	31.27	68.73	Clay
G-34	Ponnani	10.68	75.89	9.80	9.67	9.24	3.30	-0.19	0.78	0.00	6.13	30.28	63.59	Clay
G-35	Ponnani	10.63	75.78	31.40	9.56	9.33	3.09	-0.12	0.79	0.00	2.84	31.22	65.93	Clay
G-36	Azhikodu	10.18	76.11	13.50	9.14	8.46	2.19	-0.41	0.86	0.00	2.97	33.25	63.76	Clay
G-37	Alleppy	9.52	76.25	15.00	8.21	7.84	1.78	-0.14	1.63	0.00	2.48	38.39	59.13	Clay
G-38	Alleppy	9.45	76.14	37.00	8.22	7.80	1.79	-0.16	1.56	0.00	0.69	39.46	59.85	Clay
G-39	Kayamkulam	9.26	76.36	13.00	9.31	9.20	3.01	-0.04	0.68	0.00	1.40	40.49	58.11	Clay
G-40	Kayamkulam	9.09	76.32	33.00	9.12	8.93	2.91	-0.05	0.67	0.00	2.14	38.63	59.23	Clay
G-41	Vizhinjam	8.39	76.93	38.00	8.20	8.10	2.94	0.30	1.23	0.00	13.16	18.84	67.99	Sandy clay
G-42	Kanyakumari	8.08	77.82	23.00	8.93	8.76	3.22	0.01	0.68	0.00	4.32	42.41	53.27	Silty Clay
*The grain size and statistical parameters given are for offshore samples only														

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