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1.1 Rare Earth Elements

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

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

[\text{[Xe]} = \text{configuration of xenon: 1s}^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6]  

Table 1.1 Atomic weight and ground state electronic configurations of rare earth elements. (* Does not exist in nature).
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They form a very coherent group, although two elements Ce and Eu may develop anomalies due to changes in their oxidation states. Pm, a lanthanide between Nd and Sm which can be produced by nuclear reactions, does not exist in nature in significant concentrations.

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

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

1.2 Chemical properties

REEs are difficult to separate because of their chemical similarity. The chemical similarity is with regard to the electronic configuration of the atoms and ions of the individual elements (Möller, 1968)
Lanthanum has an outer electronic configuration in the ground state of $5d^16s^2$, but the next element, Ce has an electron in the 4f sub-shell (Table 1.1). The following elements have the electrons entering the 4f sub-shell, until at ytterbium the 4f sub-shell is filled. The 4f electrons are well shielded by the eight electrons in the $5s^2$ and $5p^6$ sub-shells, so that they are not significantly involved in chemical reactions. Hence, any difference in the number of electrons in the 4f sub-shell does not lead to much difference in chemical behaviour, nor to significant ligand field affects. The REEs, therefore, tend to occur in any natural forms as a group rather than singly or as a combination of a few of their number (Henderson, 1984).

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

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

The lanthanides were originally called rare earth elements. The word 'earth' was used because they occurred as oxides (which in early usage meant earth) and the word 'rare' was used because their occurrence was believed to be very scarce. Now many more elements occur even more rarely than lanthanides. Hence, although they are not abundant by any means, they are not considered to be rare in the sense in which this word was used before. The most commonly occurring lanthanide is Ce which constitutes about $3 \times 10^{-4}$ percent of the earth's crust. For example, Ce is more abundant than tin in the earth's crust. Even the scarcest rare earths are more abundant than the platinum group elements. They are much more abundant than Au (4 ppb), Ag (70 ppb) and U (ppm) in the crust (Möller, 1989). Neodymium is more abundant than lead.

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

1.3.1 Rare earth minerals

The concentration of the REEs during igneous rock formation (particularly granites and nepheline syenites) and in pegmatites leads to the crystallization of many rare earth minerals. Among the more important are the following: Yttriofluorite (CaF$_2$, YF$_3$), Bastnaesite (CeF)CO$_3$, Allanite (Ca,FeCeAl) silicate, monazite (LREE,Th)PO$_4$, etc. The principal source of the REEs is the mineral monazite, occurring in beach sand deposits.
Recovery of the rare earths is a by-product of the extraction of thorium. (Taylor, 1972).

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

1.4 Lanthanides in nature

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

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

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

1.5 Oceanic system

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

1.5.1 REE supply to the Oceans

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

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

1.5.2 REEs in seawater

The oceans are heterogenous both on small and large scales with respect to REEs concentration, because the residence times of REEs are shorter than the mixing time of the oceans (~1000yrs). The REEs are minor constituents of seawater, having concentrations of only a few nanograms per litre. Unlike river water, seawater is markedly depleted in Ce. Goldberg (1961) proposed that Ce$^{3+}$ in the oceans is oxidized to Ce$^{4+}$ and is precipitated from solution as CeO$_2$, while the other REEs remain in the 3+ state and are lost from solution without discernible fractionation of other individual REE. This fractionation of Ce is due to its rapid removal, relative to the other REEs, from the oceans, as indicated by the residence times of the REEs (Table 1.2). Carpenter and Grant (1967) also supported that Ce$^{3+}$ rapidly forms colloidal Ceric hydroxide in seawater with a pH of 8 or more.
<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. (ng/l)</th>
<th>Residence time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>3</td>
<td>440</td>
</tr>
<tr>
<td>Ce</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>Pr</td>
<td>0.6</td>
<td>320</td>
</tr>
<tr>
<td>Nd</td>
<td>3</td>
<td>270</td>
</tr>
<tr>
<td>Sm</td>
<td>0.05</td>
<td>180</td>
</tr>
<tr>
<td>Eu</td>
<td>0.01</td>
<td>300</td>
</tr>
<tr>
<td>Gd</td>
<td>0.7</td>
<td>260</td>
</tr>
<tr>
<td>Dy</td>
<td>0.9</td>
<td>460</td>
</tr>
<tr>
<td>Ho</td>
<td>0.2</td>
<td>530</td>
</tr>
<tr>
<td>Er</td>
<td>0.8</td>
<td>690</td>
</tr>
<tr>
<td>Tm</td>
<td>0.2</td>
<td>1800</td>
</tr>
<tr>
<td>Yb</td>
<td>0.8</td>
<td>530</td>
</tr>
<tr>
<td>Lu</td>
<td>0.2</td>
<td>450</td>
</tr>
</tbody>
</table>

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

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

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

1.5.3 REE contents of sediments and sedimentary rocks

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

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

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

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

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

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

1.7 Aim and Scope of present study

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

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

The detailed objectives of the study are:

1) To estimate distribution pattern of REEs, Th and U in the sediments along the Eastern Arabian Sea
2) To study the behaviour of Eu and Ce with respect to their neighbouring elements in view of their occurrence in multiple oxidation states, in the study area.
3) Inter-element relation of rare earth elements with other major elements diagnostic of redox, provenance and other geochemical processes
4) To study the north-south variation of REEs along the western continental margin and relate them to local geological and oceanographic processes
5) To study the depth wise variation of sedimental REEs from near shore areas (30m) to offshore depths (200m)

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

Andaman Backarc basin

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

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

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


Goldstein S.J. and S.B.Jacobsen 1988. Rare earth elements in river waters. Earth Planet Sci. Lett. 89. 35-47


Chapter 1


