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Focus Paper

Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact

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ABSTRACT

Rare earth elements (REE) include the lanthanide series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) plus Sc and Y. Currently these metals have become very critical to several modern technologies ranging from cell phones and televisions to LED light bulbs and wind turbines. This article summarizes the occurrence of these metals in the Earth's crust, their mineralogy, different types of deposits both on land and oceans from the standpoint of the new data with more examples from the Indian subcontinent. In addition to their utility to understand the formation of the major Earth reservoirs, multi-faceted updates on the applications of REE in agriculture and medicine including new emerging ones are presented. Environmental hazards including human health issues due to REE mining and large-scale dumping of e-waste containing significant concentrations of REE are summarized. New strategies for the future supply of REE including recent developments in the extraction of REE from coal fired ash and recycling from e-waste are presented. Recent developments in individual REE separation technologies in both metallurgical and recycling operations have been highlighted. An outline of the analytical methods for their precise and accurate determinations required in all these studies, such as, X-ray fluorescence spectrometry (XRF), laser induced breakdown spectroscopy (LIBS), instrumental neutron activation analysis (INAA), inductively coupled plasma optical emission spectrometry (ICP-OES), glow discharge mass spectrometry (GD-MS), inductively coupled plasma mass spectrometry (including ICP-MS, ICP-TOF-MS, HR-ICP-MS with laser ablation as well as solution nebulization) and other instrumental techniques, in different types of materials are presented.

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1. Introduction

Rare-earth elements (hereinafter referred to as REE) are a group of seventeen chemical elements in the periodic table, in particular the fifteen lanthanides as well as yttrium and scandium as defined by the International Union of Pure and Applied Chemistry (IUPAC). Scandium and yttrium are considered REE since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. All REE occur in nature but not in pure metal form, although Promethium, the rarest, only occurs in trace quantities in natural materials as it has no long-lived or stable isotopes (Castor and Hendrik, 2006). In lanthanide atoms, the configuration of the valence electrons of the outermost shell is the same for all the species while the 4f orbitals are progressively filled with increasing atomic number. Screening of the 4f orbitals leads to the extremely similar physical and chemical properties of the elements. Another related consequence is the so-called "lanthanide contraction" in which the ionic radius progressively decreases from La^{3+} (1.06 Å) to Lu^{3+} (0.85 Å). REE are the elements that have become extremely important to our world of technology owing to their unique magnetic, phosphorescent, and catalytic properties. These elements are critical to technologies ranging from cell phones and televisions to LED light bulbs and wind turbines. The estimated average concentration of the REE in the Earth's crust which ranges from around 130 μg/g to 240 μg/g which is actually significantly higher than other commonly exploited elements, and much higher than their respective chondritic abundances (Zepf, 2013). Table 1 presents the average abundances of REE (in μg/g) in Earth's crust in comparison with chondritic abundances. This review aims to provide an updated understanding of the global scenario of REE, starting from their applications in high technology products, occurrence, different types of economic deposits both on land and oceans, their

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Table 1
Average abundance (in μg/g) of REE in the Earth's crust in comparison with chondritic abundances.

Elements	Taylor and MeLennan (1985)	Wedepohl (1995)	Lide (1997)	Chondritic abundances	
				Wakita et al. (1971)	Pourmand et al. (2012)
La	16.0	30	39	0.34	0.2469
Ce	33.0	60	66.5	0.91	0.6321
Pr	3.9	6.7	9.2	0.121	0.0959
Nd	16.0	27	41.5	0.64	0.4854
Sm	3.5	5.3	7.05	0.195	0.1556
Eu	1.1	1.3	2	0.073	0.0599
Gd	3.3	4	6.2	0.26	0.2093
Tb	0.6	0.65	1.2	0.047	0.0378
Dy	3.7	3.8	5.2	0.30	0.2577
Ho	0.8	0.8	1.3	0.078	0.0554
Er	2.2	2.1	3.5	0.20	0.1667
Tm	0.3	0.3	0.52	0.032	0.0261
Yb	2.2	2	3.2	0.22	0.1694
Lu	0.3	0.35	0.8	0.034	0.0256
Y	20.0	24	33	-	1.395
Sc	30.0	16	22	-	5.493
Total	136.9	184.3	242.17	-	9.5118

Note: - stands for not available.

behavior in different geological systems, state-of-the-art chemical characterization techniques and recycling. Other aspects such as their applications in agriculture, medicine together with the environmental effects and search for alternatives to REE in different applications are also presented.

2. High-technology applications of REE

During the last three decades, there has been an explosion in the applications of REE and their alloys in several technology devices such as computer memory, DVDs, rechargeable batteries, autocatalytic converters, super magnets, mobile phones, LED lighting, superconductors, glass additives, fluorescent materials, phosphate binding agents, solar panels and magnetic resonance imaging (MRI) agents. These metals are being consumed this way for a variety of applications at an unprecedented rate. Since they are extremely important ingredients in all high-technology gadgets, these elements are called *"The Vitamins of Modern Industry"* (http://metalpedia.asianmetal.com/metal/rare_earth/application.shtml). For example, Nd is extensively applied in super magnets for disk drives, Ce is critical ingredient in autocatalyts and all REE are used in making the flat-panel TVs. Several compounds of REE are in smart-batteries that power every electric vehicles and hybrid-electric vehicles. Because of their unique physical, chemical, magnetic, luminescent properties, these elements help to make many technological advantages such as performing at reduced energy consumption, greater efficiency, miniaturization, speed, durability and thermal stability. In recent years, their demand is particularly on rise in energy efficient gadgets (green technology) which are faster, lighter, smaller and more efficient. These technologies are even helping the analytical instruments to become smaller and more efficient (Balaram, 2016a). Table 2 summarizes the extensive applications of REE in the modern technological gadgets in different areas. Because of the emerging green technologies in a big way, the REE application boom would continue in near future also. Fig. 1 presents an overview of REE production by different countries and utilization for different applications in 2017. It is very interesting to see that these applications are dominated by their use in autocatalytic converters and industrial catalysts. Dutt et al. (2016) predicted that global REE demand is slated to grow at annual rate of 5% by 2020 and Graede (2015) in a three-dimensional graphic

Table 2
Some examples of how REE are being utilized in the world today in different areas (http://www.namibiarareearths.com/rare-earths-industry.asp).

Area	Applications
Electronics	Television screens, computers, cell phones, silicon chips, monitor displays, long-life rechargeable batteries, camera lenses, light emitting diodes (LEDs), compact fluorescent lamps (CFLs), baggage scanners, marine propulsion systems.
Manufacturing	High strength magnets, metal alloys, stress gauges, ceramic pigments, colorants in glassware, chemical oxidizing agent, polishing powders, plastics creation, as additives for strengthening other metals, automotive catalytic converters.
Medical Science	Portable X-ray machines, X-ray tubes, magnetic resonance imagery (MRI) contrast agents, nuclear medicine imaging, cancer treatment applications, and for genetic screening tests, medical and dental lasers.
Technology	Lasers, optical glass, fiber optics, masers, radar detection devices, nuclear fuel rods, mercury-vapor lamps, highly reflective glass, computer memory, nuclear batteries, high temperature superconductors.
Renewable Energy	Hybrid automobiles, wind turbines, next generation rechargeable batteries, biofuel catalysts.
Others	The europium is being used as a way to identify legitimate bills for the Euro bill supply and to dissuade counterfeiting. An estimated 1 kg of REE can be found inside a typical hybrid automobile.
	Holmium has the highest magnetic strength of any element and is used to create extremely powerful magnets. This application can reduce the weight of many motors.

indicated that there will be scarcity and supply risk for Eu, Dy and Er in addition to several other metals in the near future. This estimation is based on their scores in three areas namely supply risk, environmental implications, and vulnerability to supply restrictions (Fig. 2). Thus, the increasing global demand for these elements is currently generating lot of interest among exploration geochemists as well as technology developers especially because of their very important role in green applications such as hybrid cars, electric car batteries and wind turbines under the backdrop of climate change and global warming.

3. Distribution of REE in the Earth's crust and mineralogy

In nature, REE do not exist as individual native metals such as gold, copper and silver because of their reactivity, instead occur together in numerous ore/accessory minerals as either minor or major constituents. Though REE are found in a wide range of minerals, including silicates, carbonates, oxides and phosphates, they do not fit into most mineral structures and can only be found in a few geological environments. The principal economic sources of REE minerals are bastnaesite, monazite, and loparite and the lateritic ion-adsorption clays. There are over 250 minerals which contain REE as important constituents in their chemical formula and crystal structure (Dostal, 2017). Table 3 presents the list of some important REE bearing minerals associated with REE deposits.

4. REE exploration

Currently the world reserves of REE by principal countries such as China, Brazil, Vietnam, Russia and India, stand at about 130 million tonnes (U.S. Geological Survey, 2018) (Table 4). These resources are primarily from four geologic environments: carbonatites, alkaline igneous systems, ion-adsorption clay deposits, and monazite-xenotime-bearing placer deposits. China with one-third of world's REE reserves, is still the world leader in REE exploration and production. Before REE mining boom in China, the US dominated the global market. Mountain Pass initiated operations in 1965 and was the leading producer worldwide for decades

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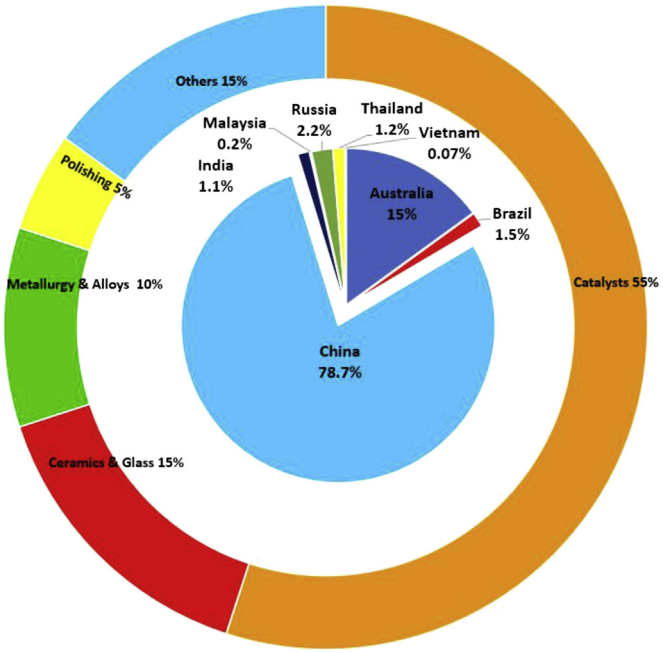


Figure 1. REE production by different countries and utilization for different applications in 2017 (https://minerals.usgs.gov/minerals/pubs/mcs/2017/mcs2017.pdf).

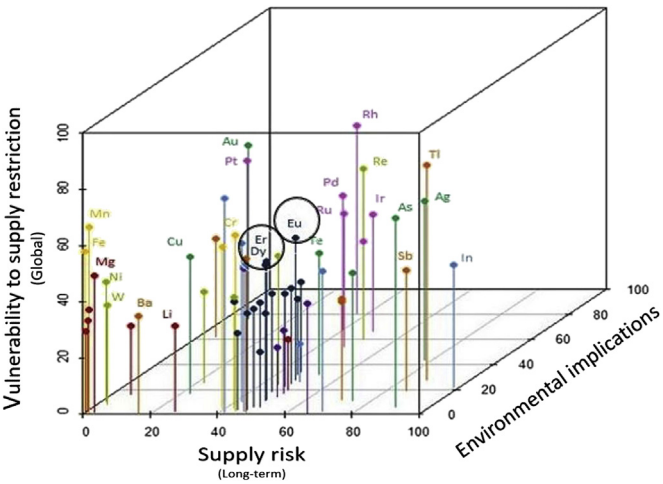


Figure 2. Estimated supply risk for Eu, Dy and Er in addition to several other metals in the near future (Graede, 2015).

(Barakos, 2017). However, mining activities stopped in 1998, mainly due to the competition from China as well as in response to environmental issues in the surrounding area of Mountain Pass (Ali, 2014; Mancheri, 2015). Apart from Mountain Pass, significant exploration projects in the United States include the Bear Lodge, the Bokan-Dotson Ridge, the Round Top and the La Paz projects (Barakos et al., 2018). While the exploration studies worldwide are mainly concentrated on Au, Ag, Cu, platinum group elements (PGE), Ni, Cu, Cr, Li, U, Zn, K and Pb, some countries in Africa and Asia Pacific showed interest in REE exploration in 2017. Apart from China and India, countries such as Kazakhstan, Kyrgyzstan, Tajikistan, Uzbekistan, and Turkmenistan have also identified significant REE-bearing mineral occurrences including alkaline igneous rocks and carbonatites (Kogarko et al., 1995; Mihalasky et al., 2018). There has been continued interest in exploration for

Table 3
Names and formulae of some important REE-bearing minerals associated with REE deposits (Dostal, 2017).

Mineral	Formula
Allanite	$(Y,Ln,Ca)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$
Apatite	$(Ca,Ln)_5(PO_4)_3(F,Cl,OH)$
Bastnaesite	$(Ln,Y)\ (CO_3)F$
Eudialyte	$Na_4(Ca,Ln)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH,Cl)_2$
Fergusonite	$(Ln,Y)NbO_4$
Gittinsite	$CaZrSi_2O_7$
Ilmoriite	$Y_2(SiO_4)\ (CO_3)$
Kainosite	$Ca_2(Y,Ln)_2Si_4O_{12}(CO_3).H_2O$
Loparite	$(Ln,Na,Ca)\ (Ti,Nb)O_3$
Monazite	$(Ln,Th)PO_4$
Mosandrite	$(Na,Ca)_3Ca_3Ln\ (Ti,Nb,Zr)\ (Si_2O_7)_2(O,OH,F)_4$
Parisite	$Ca\ (Ln)_2(CO_3)_3F_2$
Pyrochlore	$(Ca,Na,Ln)_2Nb_2O_6(OH,F)$
Rinkite (rinkolite)	$(Ca,Ln)_4Na(Na,Ca)_2Ti(Si_2O_7)_2(O,F)_2$
Steenstrupine	$Na_{14}Ln_6Mn_2Fe_2(Zr,Th)\ (Si_6O_{18})_2(PO_4)_7.3H_2O$
Synchysite	$Ca\ (Ln)\ (CO_3)_2F$
Xenotime	YPO_4
Zircon	$(Zr,Ln)SiO_4$

Table 4
World reserves of REE by principal countries (U. S. Geological Survey, 2018).

Country	Reserves in tonnes (in terms of REO)	% Share
Australia	3,400,000	2.56
Brazil	22,000,000	16.67
Canada	830,000	0.63
China	44,000,000	33.33
Greenland	1,500,000	1.14
India	6,900,000	5.23
Malaysia	30,000	0.02
Malawi	140,000	0.11
Russia	18,000,000	13.64
South Africa	860,000	0.65
Vietnam	22,000,000	16.67
USA	1,400,000	1.06
World Reserves	**132,000,000**	-

REO = Rare Earth Element Oxide.

REE worldwide. In an annual exploration review, Wilburn and Karl (2018) reported that the United States Geological Survey (USGS) conducted extensive hyperspectral surveys in Alaska and evaluated the mineral potential for REE in addition to other metal deposits throughout the State in 2017. India which account for about 5% of the world's REE reserves, currently exploits its primary resource, monazite. Significant REE minerals found in India include ilmenite, sillimanite, garnet, zircon, monazite and rutile, collectively called Beach Sand Minerals (BSM). India has almost 35% of the world's total beach sand mineral deposits. The REE minerals in India predominantly contain light REE (LREE). The Geological Survey of India (GSI) has taken up number of REE exploration projects across the country during the last 5 years. The search for REE mineralization includes identification of anomalous concentration zones on the basis systematic geological mapping (SGM) at scale 1:50,000, specialized thematic mapping (STM) at scale 1:25,000, and National Geochemical Mapping (NGCM) at scale 1:50,000 and delineation of target zones for enhanced potential through reconnaissance stage investigations (https://www.gsi.gov.in). In recent times, GSI has increased its efforts for the exploration of REE in addition to base metals and rare metals, and also for the development of cost-effective extraction and separation methods. Major targets are alkaline rocks, skarns, carbonatites, peraluminous granitoids and their derivatives like pegmatites, quartz-veins and greisens which host primary REE deposits in addition to placers and residual weathering deposits derived from primary deposits. Xenotime deposits (xenotime is a rare earth phosphate mineral which

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is a rich source of yttrium and heavy rare earths) in Madhya Pradesh, carbonatite-alkaline complex in Ambadongar, Gujarat, polymetallic mineralization in Siwana Ring Complex, Rajasthan (Banerjee et al., 2014) are some of the promising areas for REE exploration and exploitation. Monazite in the beach and inland placer deposits in India have been estimated to be 11.935 million tonnes in 2016 with over 30% of the resources coming from the coastal state of Andhra Pradesh (IBM Report, 2018). During the last quarter century, the demand for REE skyrocketed because of innumerable number of applications. Other countries with notable production are US, Australia, Brazil, India, Malaysia, Russia, Thailand and Vietnam. Fig. 1 presents the estimated global REE production in 2017. However, China has restricted its exports since 2010 for reasons unknown. Although there are lots of research and development efforts going on to find out a cheaper substitution for the REE (e.g. Pavel et al., 2017), there are no significant breakthroughs yet in this direction. Because of these reasons, the REE demand increased manifold and currently vigorous exploration efforts are going on to find out new REE ore deposits. However, due to their geochemical characteristics, REE are very dispersed and not usually found concentrated as rare earth minerals in economically exploitable ore deposits. Hence, it is unusual to find them in quantities significant enough to form economic ore deposits. The world's largest REE deposits are mostly bound to carbonatites or their altered equivalents (Laznicka, 2010). Detecting possible future deposits and determining the concentrations and relative enrichment of REE in carbonatites, silico-carbonatites, peralkaline granites and pegmatites are of interest for mineral exploration and mining processes. However, commercially operating mines around the world mainly extract bastnaesite, monazite and xenotime ores. Mainly, monazite from beach placers is mined in India as the principal ore mineral for REE, although xenotime holds out some prospect for the future. Of India's estimated reserve of 5 million tons of monazite, 70%–75% which occurs in beach placers and the rest in the inland and offshore areas. Monazite content of beach sands may be up to 11 wt.%. Recent studies (Gonzalez et al., 2010; Kato et al., 2011; Balaram et al., 2012) have indicated that different types of seafloor sediments which harbor high concentrations of REE. It is believed that ocean bottom-REE resources are much more promising than on-land resources (Kato et al., 2011; Takaya et al., 2018).

4.1. Types of REE deposits

Although REE are relatively abundant in the Earth's crust, unlike most other metals, they are rarely concentrated into mineable ore deposits. Potential deposits of the REE can be divided into primary and secondary deposits. Primary deposits are those formed by magmatic, hydrothermal and/or metamorphic processes. These deposits are most commonly associated with alkaline igneous rocks and carbonatites, emplaced into extensional settings. Secondary deposits are those formed by erosion and weathering and may include placers, laterites and bauxites. Within these two groups REE deposits can be further subdivided depending on their genetic associations, mineralogy and form of occurrences. As REE deposits appear in a wide variety of geological environments, it is not very easy to classify them into different categories. Sowerbutts (2017) classified the economically important REE deposits into four categories, however, in view of significant quantities of these elements in coal and marine sediments, in the present study, the REE deposits have been divided into the following five categories, i.e., (i) Alkaline igneous rocks: pegmatites and carbonatites, (ii) residual deposits, (iii) heavy mineral placers, (iv) REE in coal and (v) REE in the sediments of continental shelf and Ocean bottom. These will be considered in little more detailed way in the following.

4.1.1. Alkaline igneous REE deposits

Alkaline igneous rocks are formed by the partial melting of deep mantle rocks, which subsequently rise and cool within the Earth's crust. Typically, an alkaline magma is enriched in not just REE but also Zr, Nb, Sr, Ba, and Li. As the magma ascends it changes chemically in response to a complex interaction of factors including temperature, pressure, and the chemistry of the surrounding rocks. This complex interaction results in the formation of great variety of REE deposits (Ray and Shukla, 2004). The hosts are differentiated rocks ranging from nepheline syenites and trachytes to peralkaline granites. These complexes usually occur in continental within-plate tectonic settings associated with rifts, faults, or hotspot magmatism. The REE mineralization is also found in layered alkaline complexes, granitic stocks, and late-stages dikes and rarely trachytic volcanic and volcaniclastic deposits (Dostal, 2017). Examples of REE deposits associated with alkaline igneous rocks include Mountain Pass, California; China's Bayan Obo; and Ytter by, Sweden. China's Bayan Obo deposit, the largest REE deposit, is a high-grade, igneous related carbonatite deposit that sources 80% of the world's LREE (Verplanck et al., 2014). Carbonatites of the Sung Valley ultramafic–alkaline–carbonatite Complex, West Jaintia Hills and East Khasi Hills districts of Meghalaya, North East India has been identified by Singh et al. (2014) with encouraging values for REE (ΣLREE values range from 895.17 μg/g to 1264.85 μg/g and ΣHREE values range from 60.98 μg/g to 81.92 μg/g). Cut-off grade in mining metallurgical operations are influenced by economic indicators such as market price of both the primary product and the by-product, mining and processing costs, metallurgical recovery tonnage grade distribution (Nieto and Zhang, 2013). Hence, it is very difficult to mention the cut-off grade of the ore. The Saranu deposit located in Rajasthan, is a significant carbonatite deposit within India that carries notable concentrations of REE. The deposit contains $\geq$5.5% REO (rare earth oxides) and they are hosted in carbonatite dikes of about 10 cm wide (Wall and Mariano, 1996). LREE minerals such as bastnäsite, parisite, and synchysite have been reported from the Amba Dongar carbonatite complex, Gujarat (Doroshkevich et al., 2009). By using geological mapping and grid channel geochemical sampling methods, Bhushan and Kumar (2013) discovered carbonatite plugs, sills and dykes hosting REE deposits at Kamthai (very close to Saranu deposit), Barmer district, Rajasthan, India, with potential REE resources of 4.91 Mt and estimated up to 84 m depth having highest value of LREE is 17.31% and the mean grade is 3.33%. In a subsequent study of these carbonatites as well as host ijolite plug of Kamthai, Bhushan (2015) attributed the genesis of this deposit to mantle 'hot spot' activity coeval with the Deccan volcanism. Recently Bhushan and Somani (2018) made an extensive study on the REE and Y potentials of Neoproterozoic peralkaline Siwana granite of Malani igneous suite, Barmer district, Rajasthan. They also made an extensive REE mineral characterization of the suite with well exposed and outcrops and opined that the area is well suited for open cost mining. Total REE content of Neoproterozoic Peralkaline Siwana granite of Malani igneous suit, is ranging from 2% to 2.5%. The economic viability will greatly depend upon the mineralogy and leachability and separation through metallurgical test. Even 50% extraction from the ore will be economical due to high price of HREE. As the area is well exposed and outcrops have high relief, the cost through opencast mining will be minimum (Bhushan and Somani, 2018).

4.1.2. Residual deposits

Residual deposits formed from deep weathering of igneous rocks, pegmatites, iron-oxide copper-gold deposits. Intense weathering of carbonatite and peralkaline intrusives may form concentrated residual deposits of REE minerals. Examples include REE-laterite in south China resulting from weathering of tin granite.

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Ion-adsorption ores which come under this category are known only from China. Appreciable area of North East India experiences climatic conditions favorable for the development of thick lateritic profile and is promising for this type of REE deposits (Singh et al., 2014). Bauxite, the principal ore of aluminum formed during the weathering of various kinds of aluminosilicate source rocks (Valeton, 1972), is also found to be a rich source for REE. Bauxite residue (red mud) is the solid residue generated in the Bayer process for aluminum production. This waste residue as well as selected bauxite deposits are potential sources of REE (Vind et al., 2018).

4.1.3. Heavy mineral placer deposits

Potentially useful concentrations of REE-bearing minerals are also found in placer deposits. Most placer accumulations with significant amounts of REE minerals are Tertiary or Quaternary deposits derived from source areas that include granitic rocks or high-grade metamorphic rocks; however, paleo placer deposits that are as old as Precambrian, also contain REE resources. Monazite [$(Ce,Th)PO_4$], a common REE-bearing accessory mineral in igneous, metamorphic, and sedimentary rocks, may be concentrated with other heavy minerals in placer deposits. Monazite is an important REE ore and most monazite ore deposits that are economically viable REE resources. Monazite includes cerium, and associated light REE and heavy REE such as Tb, Dy and Gd tend to be rarer, smaller, and less concentrated. In India, monazite is the principal source of light REE. As a result, for HREE, India depends heavily on imports. Examples of placer deposits of REE include tin-rich river placers in Malaysia; paleo-placers in Witwatersrand, South Africa; Elliot Lake, Ontario, and beach sand deposits of Kerala, Andhra Pradesh, Tamil Nadu and Odisha in India. Though China, Malaysia and India are the countries involved at present in the processing of monazite, Brazil and Russia are also entering in to monazite processing. Palaparthi et al. (2017) have carried out a comprehensive study to determine the radioelement and REE concentrations in beach placer deposits at selected locations along the eastern coast of Andhra Pradesh in India to understand their economic potential. Small concentrations of thorium and uranium are making monazite a restricted 'atomic' mineral in India. As a result, private firms are not being allowed processing of monazite at present.

4.1.4. REE in coal deposits

As the gap between REE global demand and supply increases, the search for their alternative resources has become more and more important, especially for the countries which depend highly on their import. Coal fly ash, which is considered as waste, has now been regarded as the possible source for many elements, including REE (Franus et al., 2015). This is because the REE concentrations in many coals or coal ashes are equal to or higher than those found in conventional REE ores. For example, in coal samples from the Mazino Coal Mine, Tabas Coalfield, Iran, ΣREE range of 16.4–184 μg/g with average of 88.9 μg/g (Pazand, 2015). In a recent study, Sahadev et al. (2018) have observed considerably low REE in the Indian coal samples from the North Eastern Region (NER) in comparison to world average coal. On the other hand, in world coal ash ΣREE value is ~404 μg/g (Dai et al., 2016). In fact, even much higher values up to 1358 μg/g of REE (including Y) have been reported in the literature (Hower et al., 2016). This would offer the potential to reduce our dependence on others for these critical elements and also create new industries in regions where coal has played an important economic role. The possible recovery of REE from abundant coal and coal ash is an exciting new research area, representing a dramatic paradigm shift for coal (Franus et al., 2015). Some scientists believe that the future of REE may lie with coal (Alvin et al., 2017). Currently several studies are underway to optimize the extraction of REE from coal fly ash (e.g. Franus et al., 2015; Taggart et al., 2018).

4.1.5. REE in the sediments of continental shelf and ocean bottom

Mineral resources of the continental shelf are similar to those of contiguous land. Minerals eroded from the land may be concentrated in placer deposits in beaches along the coast and similar placer deposits can be expected farther offshore, beneath the ocean. Continental shelves also contain huge deposits of phosphorite (phosphate rock or rock phosphate), a non-detrital sedimentary rock which is also an important source of REE. Recent studies of marine phosphorite deposits reveal that there are significant quantities of REE contained within the phosphorites (Mazumdar et al., 1999; Nath et al., 2000; Khan et al., 2012; Dar et al., 2014; Li and Schieber, 2015). Phosphorite deposits form as chemical precipitates on continental shelves at relatively shallower depths in oceans (Fig. 3) unlike manganese nodules and cobalt crusts. Upwelling of cold, phosphate rich waters causes warming and decreases in solubility, and are deposited. It has been recognized that REE get enriched in the francolite mineral phase of phosphorites where REE substitute for Ca in the francolite lattice (Jarvis, 1994). Some of the phosphorite deposits contain ΣREE up to 2000 μg/g, although composition of these rocks mostly depends on their type and origin. Emsbo et al. (2015) while presenting the chemical analysis data of 23 sedimentary phosphate deposits (phosphorites) with ΣREE up to 18,000 μg/g and ΣHREE up to 7000 μg/g, suggest that phosphorite deposits are highly potential resources for REE than most conventional REE deposits.

Recent studies (Hein et al., 2010; Kato et al., 2011; Balaram et al., 2012; Zhong et al., 2018) also indicate that significant REE resources are available in ocean bottom sediments. There are essentially three types of REE resource in deep oceans: polymetallic nodules, ferromanganese crusts (cobalt crusts) and deep-sea muds (Fig. 3). Polymetallic nodule deposits form on the sediment-covered abyssal plains (at water depth of 4500–6000 m) and occur in surficial seafloor sediments in abyssal plain muds, mainly in the Pacific and Indian Oceans (Nath et al., 1994). Cobalt crusts (more precisely referred to as cobalt-rich ferromanganese crusts) are found throughout the ocean basins on seamounts, ridges, and plateaus on hard-rock substrates and occur as a surface encrustation on seamounts and rock outcrops in all oceans (Fig. 3), but with the richest deposits found in the western Pacific; and seafloor massive sulfides (SMS) that are formed at seafloor hot springs along ocean plate boundaries (Paropkari et al., 2010; Zeng et al., 2015). The compositions of these bottom sediments reflect the proportions of influxes of genetically different materials: hydrogenic, biogenic, hydrothermal, volcanogenic, and lithogenic (Banakar and Borole, 1991; Nath et al., 1992). Out of these two types, cobalt crust assumes lot of significance from the REE point of view. They form by precipitation from cold ambient bottom waters at depths typically of about 1000–3000 m and the enrichment of REE is controlled mainly by the sorption of ferromanganese oxides and clay minerals in the crusts as well as nodules. The crusts grow at extremely slow rates, about 1–7 mm/Ma and contain high concentrations of strategically and economically important metal (e.g. Co, Ti, Ce, Zr, Ni, Pt, Mo, Te, Cu, W) besides containing very high amounts of REE. There are essentially two types of ferromanganese crusts; hydrogenous (normally continuous) and hydrothermal (mostly episodic) in origin. REE patters are useful in distinguishing these two types of deposits (Prakash et al., 2012). These ocean bottom sediments are found to contain surprisingly high amounts of REE (ΣREE <2511 μg/g). Especially, the enrichment rate of Ce content is high, accounting for almost 60% of the total REE (Zhong et al., 2018). Hot plumes from hydrothermal vents brought these elements out of sea water and

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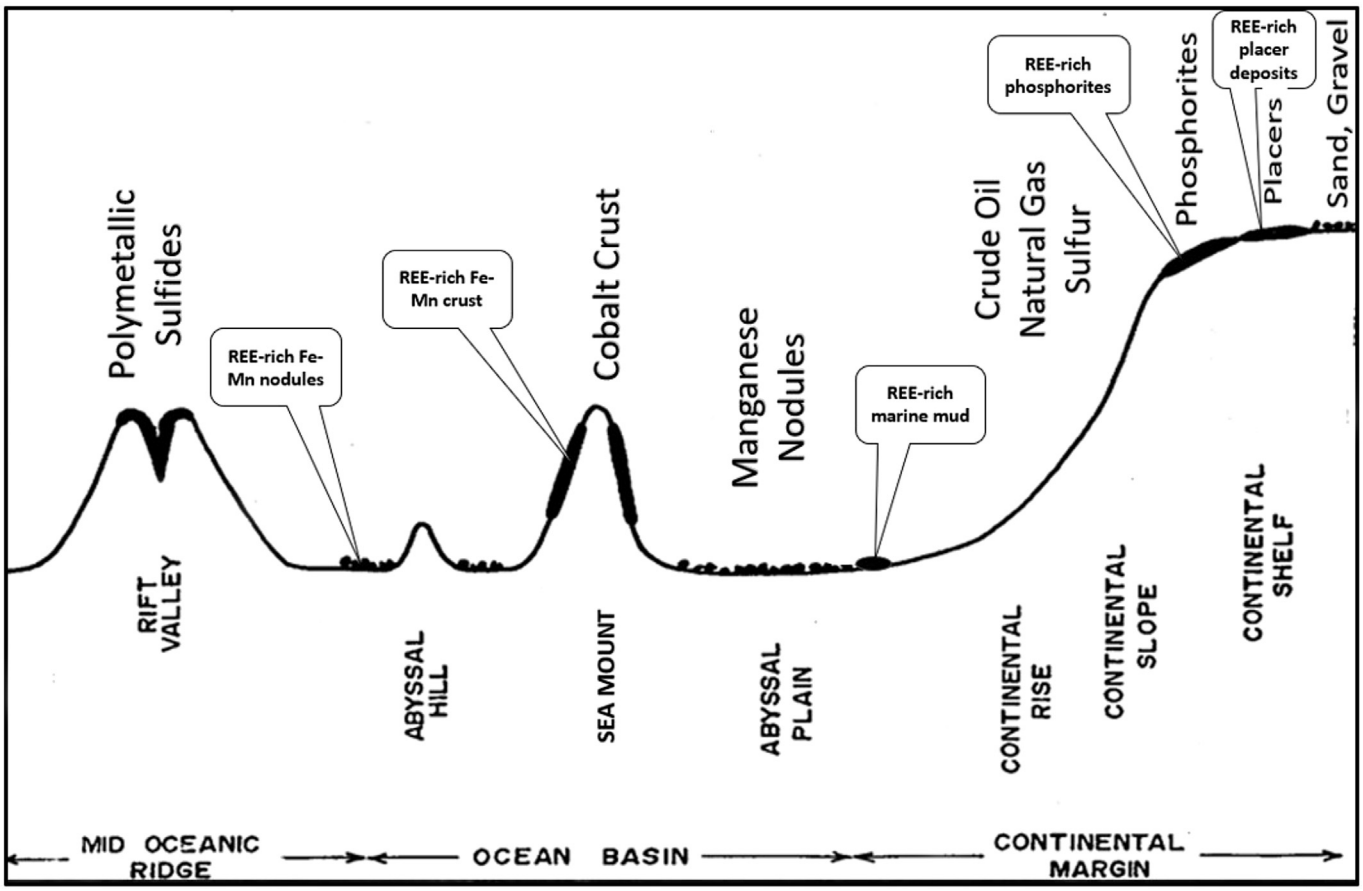


Figure 3. Occurrence of manganese nodules, cobalt crusts, marine mud and phosphorites at the ocean basins, seamounts and continental margins in the oceans.

deposited them on ocean floors, bit by bit, over tens of millions of years (Sander and Koschinsky, 2011). In an attempt to prove that the Indian Ocean also bestowed with huge resources of these valuable metals in its bottom sediments, Balaram et al. (2012) explored the seamount crust at the Afanasy Niktin Seamount (ANS) in the Indian Ocean. Subsequently, the study was extended to detailed multi-beam swath bathymetric and geochemical investigations of seamount cobalt crust (Krishna et al., 2014). Table 5 presents comparative data of ΣREE from different marine sediments of world oceans, including those of Indian Ocean.

The third significant resource for REE is the deep-sea mud which is available in abundance on the ocean bottom (Fig. 3). Yasukawa et al. (2015) analyzed 1338 deep-sea sediment samples from 19 Deep Sea Drilling Project/Ocean Drilling Program sites covering a large portion of the Indian Ocean, and constructed a new and comprehensive data set of their bulk chemical compositions, including REE, major, minor and trace elements. The resource potential of these areas particularly of the high REE-rich mud and Fe–Mn nodule fields which broadly overlap, has been highlighted. The primary challenge associated with the production of REE from these muds is the extraction process in order to make it economically feasible. Takaya et al. (2018) while reporting deep-sea mud containing over 5000 μg/g of total REE including Y from the western North Pacific Ocean near Minamitorishima Island, Japan, used an effective mineral processing method with a hydrocyclone separator which selectively separates biogenic calcium phosphate grains having high REE content (up to 22,000 μg/g). The authors also concluded that this new REE resource could be exploited in the near future. At places the Pacific mud deposit contain 100–1000

Table 5
Overview of ΣREE range (μg/g) in marine sediments from different oceans.

S. No.	Ocean	ΣREE/ΣREY range (μg/g)	Matrix	Reference
1	Afanasy Niktin Seamount (ANS) in the Eastern Equatorial Indian Ocean.	1727 –2511	Cobalt crust	Balaram et al. (2012)
2	Mid-Pacific seamount	2084	Cobalt-rich crusts	Cui et al. (2009)
3	Indian Ocean	928 –1570	Ferromanganese crust	Nath et al. (1992)
4	Indian Ocean	up to 920	Marine-mud	Yasukawa et al. (2015)
5	Scotia Sea	3400	Ferromanganese crust	Gonzalez et al. (2010)
6	Eastern South Pacific	1000 –2230	Deep sea mud	Kato et al. (2011)
7	North Pacific (east & west of Hawaiian Islands)	400 –1000	Deep sea mud	Kato et al. (2011)
8	Mid-Pacific Ocean	1178 –1434	Fe-Mn nodules	Bu et al. (2003)
9	Pacific Ocean	1326	Deep-sea manganese nodules	Piper (1974)
10	Pacific Ocean	1398	Shallow water manganese nodules	Piper (1974)

S.No.1 to 4 Cobalt Crusts, 5—6 is deep sea muds and 7—9 are Ferromanganese Nodules.

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times more REE than the world's presently known land reserves of 130 million tons of REE. According to some studies, REE resources undersea are much more promising than on-land resources. One square patch of metal-rich mud 2.3 km wide might contain enough REE to meet most of the global demand for a year. Kato et al. (2011) showed that REE and Y are readily recovered from the mud by simple acid leaching, and suggested that deep-sea mud constitutes a highly promising resource for these elements.

However, with the current state of ocean mining technology, the economic viability of deep-sea mining is questionable. If the environmental and financial factors were cleared, then deep sea mining would definitely be a feasible option for the long term.

4.1.6. Extraterrestrial REE resources

According to some recent studies (McLeod and Krekeler, 2017), the REE reserves available across the world currently will be sufficient for our day-to-day needs only for <2500 years. Based on current demand, mining operations and technologies, with an expected increase in the population and technology needs, exploration of potential extraterrestrial REE resources is inevitable, with the Earth's Moon being a logical first target, after all, the Moon was once part of the Earth and got ejected in the early history of the Solar System. While REE abundances of trace phases in lunar rocks are high, their abundances are low compared to terrestrial ores which means that there is to date, no geological evidence to support mining the Moon for REE yet. While the relative concentrations and abundances of the REE in even different mineral phases of Moon, Mars and chondritic meteorites that have been characterized to date provide crucial insights into the differentiation history of planetary objects, current and future missions to the Moon, Mars, and other nearby objects in our Solar System may yet reveal one or more extraterrestrial REE resources that one day will be utilized (Haque et al., 2014).

5. Metallurgy

Due to the rarity of an economic REE deposits, they are usually mined as a co-product or a by-product to another material. For example, the primary product of Bayan Obo mine in China is iron ore, but Bayan Obo also produces much of the world's REE as by product (Philip and Anderson, 2018). Today, REE-bearing carbonates (bastnäsite) and phosphates (monazite, xenotime) are commercially processed whereas the processing technologies for REE-bearing silicates require additional Research & Development (R & D) investment to make them commercialized (Paulick and Machacek, 2017). Highly efficient separation technologies have been developed for the production of high purity REE. Gupta and Krishnamurthy (2005) provided a comprehensive review of the-state-of-the-art of extractive metallurgy of REE. According to the IBM Report (2018) Indian Rare Earth Limited (IREL), Kerala mainly extracts REE from monazite at its plants. Two of these operations are located at Aluva and Chavara in the state of Kerala. The other two are located at Manavalakurichi in Tamil Nadu and at Chatrapur in Orissa. The extraction of REE usually involves the dissolution of the ore using acidic or alkaline solutions depending on the mineralogy of the REE-containing phases and reactivity of gangue phases, typically, the use of acidic solutions is more common. Depending on mineralogy, the extraction step often involves roasting of the REE ore at 400–500 °C in concentrated sulphuric acid to remove fluoride and CO_2, and to change the mineral phase to make it more water-soluble. Generally, separation techniques such as solvent extraction, ion exchange, and precipitation are often used for the recovery of REE from pregnant leach solutions (PLS) obtained from acid or alkali leaching. Solvent extraction is generally accepted as the most appropriate commercial technology for separating REE due to the need to be able to handle larger volumes. For example, ground monazite is digested with caustic sodalye to produce trisodium phosphate (TSP) and mixed hydroxide slurry. This slurry is used for production of diverse rare earth compounds. Kumari et al. (2015) reported a review on the commercial processes based on pyro-hydro or hybrid techniques as well as systematic research for process development to recover REE from monazite. Monazite concentrate obtained are processed under different condition of time, temperature and concentration using acidic or alkaline solution. They are usually processed using thermal treatment followed by REE recovery under optimized conditions of leaching and their extraction via solvent extraction, precipitation, etc. Battsengel et al. (2018) developed a method for separating LREE and HREE in apatite from pregnant leach sulfuric acid solution by employing solvent extraction and stripping techniques. Currently, the leading process for the recovery of REE from apatite would involve leaching with nitric acid. After a nitric acid leach is performed, the REE could then be precipitated through the addition of ammonia (Sandstrom and Fredriksson, 2012).

In recent times, a revolutionary technology called SuperLig® molecular recognition technology (MRT) is being increasingly used to selectively separate and recover individual REE (Izatt et al., 2017). MRT is a green chemistry method for metal separations at the molecular level utilizing nanochemistry principles. PLS derived from the dissolution of ore is treated by the SuperLig® MRT Plant, initially to separate all 16 REE from impurity metals ("gangue metals") followed by separation of individual REE with SuperLig® resins, consisting of highly metal selective ligand attached via a tether to silica gel or another substrate. The target REE will be selectively bound to the SuperLig® resin, with remaining feed solution going to raffinate. Following the column washing, resin-bound REE will be eluted and recovered in concentrated and pure form. According to authors, the MRT process features rapid kinetics of metal-ligand binding and release, simple elution chemistry, non-use of harsh chemicals/reagents/solvents, ability to recover REE present in feed solutions at μg/mL or lower levels, and minimal generation of waste (Izatt et al., 2015). Potential applications include REE recovery from primary ore, tailings, coal ash, and spent industrial feedstock such as permanent magnets, rechargeable batteries and LED lighting systems (Izatt et al., 2018).

6. Environmental impact and health effects of REE exposure

Technological innovations in addition to modern living conditions have enhanced intake of significant quantities of toxic elements in to the human body leading to health problems. Contamination of the environment by different kinds of toxic inorganic, organic, and organometallic species is one of the most serious problems in the world today. The REE group represents important elements found in the environment and need to be studied at greater depth to understand their effects on human health. Environmental scientists have been working on the ill-effects of the well-known toxic trace elements such as As, Pb, Cd, Hg and U (Sparks, 2005; Reddy et al., 2012; Rani et al., 2013). However, many other elements, which were not commonly used in the past, e.g., the REE and PGE are increasingly being used in modern industries for the production of numerous new materials, finished products and for several technological applications. Dumping of huge amounts of e-waste is facilitating the release of significant quantities of these elements along with several other toxic elements in to the subsoils and groundwater. REE are known to be more mobile in solutions rich in F^-, Cl^-, HCO_3^-, CO_3^{2-}, HPO_4^{2-}, PO_4^{3-} ions. In addition, large quantities of REE are also getting into the agricultural soils through the phosphate-based fertilizers. The use of advanced and powerful analytical techniques such as

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inductively coupled plasma mass spectrometry (ICP-MS) and high resolution-ICP-MS (HR-ICP-MS) is now helping in improving our understanding of the reactivity and mobility of these metals in near-surface environment, their bioavailability and related health effects (Wei et al., 2013; Ali, 2014; Balaram, 2016a, b). These elements which are also finding their way into different environmental pathways especially those related to the ground and surface waters, probably have their own contribution to the environmental pollution and human health. As a consequence, a new group of elements viz., REE and PGE has been added to the already existing classification of elements (Fig. 4) depending up on their function in the environment and their toxicity in terms of human health (Bott, 1995; Balaram, 2016b). Under natural conditions, REE may only become available in small amounts via the groundwater and the atmosphere, however, their increased use has enhanced the amount of REE, and has created several new routes for bioaccumulation (in plants, animals, and human beings). Background level of REE content in waters, both surface and subsoil, varies significantly and also depends mostly on the local geology. Unfortunately, maximum acceptable limits for REE in drinking water are not available from any international health organization and also there is no sufficient data available about their toxicity to human health as stated above. In a recent study, Al-Rimawi et al. (2013) have observed very high concentrations of REE and several other metals in ground water samples from south West Bank/Palestine. The authors expressed concern as most of them have no maximum acceptable limits and also there is no sufficient data about their toxicity to human health. However, Sneller et al. (2000) have reported maximum permissible concentrations for different REE in drinking water (Table 6). According authors, these limits were derived using the data on ecotoxicology and environmental chemistry.

One major contamination seen in Europe and US but not yet reported for India is related to Gd which is used as a contrasting agent in magnetic resonance imaging (MRI). After excretion from the human body with urine, it passes through waste water treatment plants (WWTPs) almost unaffected into the aquatic system. Rivers draining highly populated urban areas in countries with a highly developed health care system are, therefore, expected to carry a large positive Gd anomaly, which is supported by a growing body of data (Bau et al., 2006; Kulaksız and Bau, 2007). Such positive gadolinium anomalies have been found worldwide, in Europe (Rabiet et al., 2009; Tepe et al., 2014), USA (Verplanck et al., 2005), Asia (Zhu et al., 2004) and Australia (Lawrence et al., 2009). German researchers from the University of Münster investigated the fate of Gd-based contrast agents emitted to the environment via wastewater discharge and were able to follow it into the processed drinking water of several water plants in Germany (Birka et al., 2016a, b). On the other hand, a 20-year record of not only Gd but also the total REE concentrations in San Francisco Bay suggests that there has been considerable increase of these elements (Hatje et al., 2016).

Intense REE mining and production activities have led to significant environmental and health impacts in countries such as China, US, India, Malaysia and Brazil. Mining activities such as cutting, drilling, blasting, transportation, stockpiling, and processing can release dust containing REE, other toxic metals and chemicals into the air and surrounding water bodies which can impact local soil, wildlife and vegetation in addition to humans. More mining of REE, however, will mean more environmental degradation and human health hazards as waste disposal areas can be exposed to weathering conditions and have the potential to pollute the air, soil and water if adequate monitoring and protection measures are not utilized (Barakos et al., 2015). Some of the REE minerals contain significant amounts of radioactive elements such as uranium and thorium, which can contaminate air, water, soil and groundwater. These problems are due to insufficient environmental regulations and controls in the mining and processing areas. One of the most significant problems is the radioactivity of some ores. For example, the Bayan Obo mine (China) employs nearly 7000 workers, of which about 3000 are exposed to thorium containing airborne dust. Elevated thoron (^{220}Rn) concentrations in air are also found. Exposure to gamma radiation is significant in the mining areas (IAEA, 2011). The extensive use of

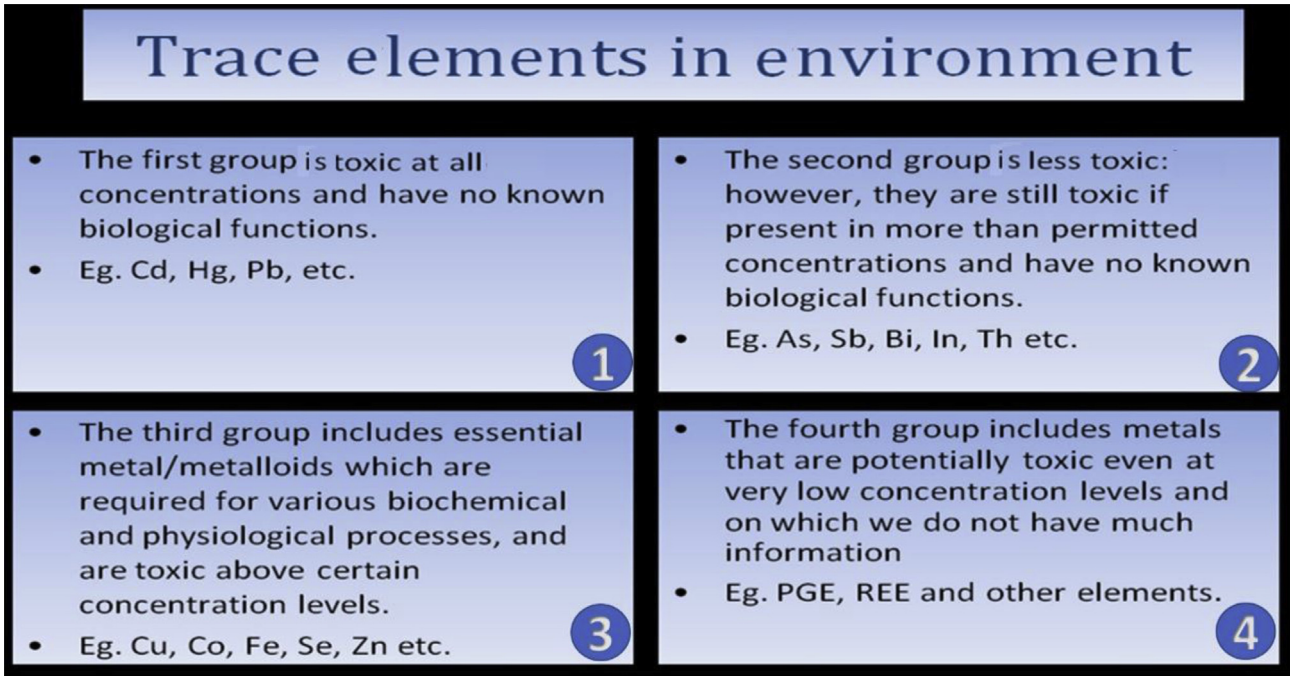


Figure 4. Trace elements have been divided into four groups depending up on their function in the environment (Bott, 1995; Balaram, 2016b).

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Table 6
Detection limits of REE obtainable by some popular instrumental analytical techniques along with maximum permissible concentrations (MPC) in drinking water.

Elements	MPC (ng/mL)	WD-XRF (μg/g)	LIBS (μg/g)	MP-AES (μg/mL)	INAA (μg/g)	ICP-OES (μg/g)	GD-MS (μg/g)	LA-ICP-MS(μg/g)	ICP-MS (ng/mL)	ICP-TOF-MS (ng/mL)	HR-ICP-MS (pg/mL)
La	10.1	3.3	10	4	0.19	0.50	<0.05	0.03	12.74	0.07	0.13
Ce	22.1	6.5	-	3	0.03	0.10	<0.05	0.04	0,61	0.06	0.19
Pr	9.1	2.7	40	-	-	0.02	<0.05	0.03	0.72	0.03	0.06
Nd	1.8	2.1	500	-	3.03	1.00	<0.05	0.07	2.45	0.18	0.24
Sm	8.2	1.7	40	3	0.08	1.30	<0.10	0.08	0.98	0.20	0.16
Eu	-	-	5	0.7	0.03	2.60	<0.05	0.03	0.37	0.06	0.02
Gd	7.1	0.7	200	4	-	0.50	<0.05	0.08	0.98	0.11	0.16
Tb	-	-	60	-	0.10	0.70	<0.05	0.03	0.07	0.02	0.02
Dy	9.3	2.7	10	-	-	0.60	<0.05	0.07	1.41	0.07	0.11
Ho	-	-	-	-	-	0.80	<0.05	0.04	0.07	0.02	0.02
Er	-	-	30	3	-	0.10	<0.05	0.05	0.11	0.05	0.08
Tm	-	-	30	-	-	0.08	<0.05	0.04	0.37	0.02	0.02
Yb	-	-	-	-	0.08	1.60	<0.10	0.07	0.37	0.10	0.08
Lu	-	-	20	-	0.04	0.40	<0.05	0.04	0.02	0.02	0.03
Y	6.4	0.4	-	-	-	0.80	-	0.06	3.68	0.06	0.30
Sc	-	-	2	-	-	0.05	-	2.04	11.03	0.39	0.23

Note: - stands for not available. HR-ICP-MS: Satyanaryanan et al. (2018a, b); ICP-TOF-MS: Balaram et al. (2013b); ICP-MS: Balaram and Rao (2003); LA-ICP-MS: Maruyama et al. (2016); ICP-AES: Amaral et al. (2017); INAA: Oliveira et al. (2003); MP-AES: Varbanova and Stefanova (2015); GD-MS: www.nu-ins.com; LIBS: Cremers and Radziemski (2006); XRF: Nakayama and Nakamura, 2005; MPC (Maximum permissible concentration limits in drinking water): Sneller et al. (2000).

REE in various modern technologies continually grow despite some knowledge about the environmental concerns of REE as they are getting released into the environment along with radionuclides. Most of the harmful effects of REE exposure to humans and their potential health effects come from the studies of mine workers and others who regularly deal with REE or their products, where exposure is typically much higher than what the general population would experience. Some studies indicate that the chemicals used in the ore processing, extraction and refining processes have been responsible for the health hazards of the workers and local residents, water pollution and destruction of farmland (Rim et al., 2013). Recent socio-environmental issue of the health impacts of REE ore processing (from both radioactive and non-radioactive contamination) in areas of China have been raised as a major concern. For example, an urban street dust of an industrial city, Zhuzhou in central China recorded very significant concentrations of REE (ΣREE ranged from 66.1 μg/g to 237.4 μg/g with an average of 115.9 μg/g) reveals the gravity of the REE pollution, particularly in industrial cities (Sun et al., 2017). This is best exemplified by the recent social and environmental conflict surrounding the development of the Lynas Advanced Materials Plant (LAMP) in Kuantan, Malaysia which led to international activism and claims of environmental and social injustice (Ali, 2014). There are also several reports of REE occupational exposure which resulted in bioaccumulation and adverse effects to respiratory tracts (Sabbioni et al., 1982; McDonald et al., 1995; Yoon et al., 2005; Rim, 2017).

In addition, contamination from dumping of huge amounts of e-waste releasing of REE in large quantities in to the subsoils and ground water is emerging very fast (Haxel et al., 2002). Each year, the electronics industry generates up to 41 million tons of e-waste, but as the number of consumers rises, and the lifespan of devices shrinks in response to demand for the newest and best, that figure could reach 50 million tons in 2018. Lange et al. (2017) studied the impact of a scrapyard of impounded vehicles on topsoil in São Paulo state, Brazil for several heavy metals and REE. Mass fractions of all elements including REE were much higher than the reference values. Hot spots were observed for most elements suggesting vehicular source.

Currently, there are substantial gaps in our understanding of the adverse effects of REE to human health, their anthropogenic levels and fate to their biogeochemical or anthropogenic cycling and their individual and additive toxicological effects. More studies are required to identify the anthropogenic sources, transfer mechanisms, bioaccumulation and their environmental behavior to minimize human health risks in future. Consequently, the adoption of new public policies and the development of more effective treatment technologies will determine the future adverse impacts of REE in aquatic systems. There is a great need to understand the toxicological properties of REE as there is a wide-spread use of these elements within agriculture and medicine and more studies and consolidation are needed to accurately assess the impact of these elements on human health (Gwenzi et al., 2018).

7. REE in agriculture

In addition, REE themselves are used in agriculture as fertilizer to improve crop growth and production and therefore leading to further increase in the concentrations of REE in soil (Tyler, 2004). In general, the mineral fertilizers (i.e., phosphate fertilizers) and soil conditioners contain macronutrients (Ca, Mg, N, P, and S), micronutrients (such as Fe and Si) and REE. In soils, the REE can also originate from local geological parent materials (Liu, 1988). REE containing micro-fertilizers are directly applied on a large-scale to plants in agriculture in China for improving the yield and quality (Guo et al., 1988; Diatloff et al., 1995). In general, the accumulated concentrations of REE have been reported to be very low. However, the accumulation capacity of a particular plant depends up on several factors such as plant species, their growing conditions, the REE content in the substrate soil or rock (Fu et al., 2001). For example, higher values were found in rice which indicated that rice has a higher accumulation ability for REE than corn. Following excessive application of REE in agriculture, there is a raising environmental concern that these elements may enter the food chain though plant uptake, which might be deleterious to human health. Some studies (Redling, 2006) confirmed very low concentrations of REE in cereal grains and no significant accumulation due to REE fertilization. Thus, grains and products made of them such as wheat flour are considered to be safe. Thomas et al. (2014) have indicated that countries like Russia and Nigeria where the natural abundance levels of REE are high in their soils will have more environmental threats arising from the increased input of REE. Close monitoring may be needed in countries where phosphate-based fertilizers (mined from monazite deposits) are applied in large scale.

8. REE in medicine

Their unique properties, such as radiation emission or magnetism, allow REE to be used in many different therapeutic and diagnostic

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applications in modern medicine. Currently there are a few major applications of REE in medicine but many more of them are on the horizon. Several studies (Zhang et al., 2000a, b; Wakabayashi et al., 2016) confirmed the antibacterial and antifungal activities of REE which is comparable to that of copper ions and these elements are beginning to find several pharmaceutical applications. For example, Gd has been used in a chelated form as a contrast agentin magnetic resonance imaging (MRI) measurements (Raju et al., 2010), though new research finds direct evidence of gadolinium deposition in neuronal tissues which can be harmful to patients (McDonald et al., 2015; Gulani et al., 2017). REE can also be used as nematicide as they can also inhibit the formation and germination of fungal spores and thus influence large number of organisms (Zhang et al., 2000b). Even the pharmaceutical samples when analyzed for inorganic impurity are found to contain appreciable amounts of especially LREE (La ~25 μg/g; Ce ~ 7 μg/g; Gd ~ 8 μg/g) when analyzed by ICP-MS (Balaram, 2016b). The implications of the presence of this range of REE concentrations in pharmaceuticals, are not clear at present. REE have been found to disease causing and occupational poisoning of local residents in mining areas, water pollution, and farmland destruction, etc. Conversely, a body of evidence has shown REE-associated antioxidant effects in the treatment of many diseases (Rim, 2016). Recently the medical and biological properties of REE have been reviewed by Panichev (2015). New medical applications for these elements are being found at an increasing rate and emerging advancements such as nanotechnology might be used to enhance their use in medicine in the future.

9. Recycling

Strategic high-tech metals such as cobalt, lithium, PGE, hafnium, tantalum, gallium and especially REE are fundamental to the world currently for the development of efficient and high-tech and environment friendly products such as electric cars which require lithium and neodymium and wind turbines requiring neodymium and dysprosium. On one hand, the world is moving towards cleaner and greener future, it is becoming extremely difficult to meet the growing demand for the REE as most of the production is located only in few countries such as China, US, Australia and India although lots of research works are going on the replacements for REE in critical technologies such as super magnets. On the other hand, mountains of e-waste rich in REE are indeed growing across the globe, but if this waste is turned into a valuable resource, this will protect human health and protect the planet's increasingly strained REE resources. Hence, many nations realized the value of recycling of e-waste, mainly scrapped electronics which is in greater demand in regions such as the EU, China and India. Essentially two options can be considered for a secure supply of REE. First from primary resources (*old mines or new deposits*, *ocean bed sediments*, *coal ash*, *etc.*) and from secondary resources (*electronic and industrial waste*). Electronic waste could in theory cover a significant part of the demand for REE. It is estimated that ~50 million metric tons of e-waste are disposed in landfills around the world each year. However, about only 12.5% of e-waste is currently being recycled for all metals.This e-waste is supposed to contain significant concentrations of REE and other precious metals such as Au, Ag, Pt, Pd and Rh. Even the recent life cycle assessments have indicated that recycling of consumer materials is a promising alternative to conventional production processes (Sprecher et al., 2014). However, recycling of REE is not easy and challenges are at every level. First of all, these elements are present in small amounts in tiny electronic parts of gadgets like mobile phones. In some materials like touch screens, these metals are evenly distributed making much more difficult to extract. Regardless of the end use, REE are not recycled in large quantities mainly because of low yield and cost, but recycling could be feasible if recycling becomes a mandate or the prices of REE go extraordinarily very high. In order to reduce future REE criticality, several studies are going on globally for cost-effective recovering REE from e-waste (Bogart et al., 2015, 2016; Fang et al., 2017; Nguyen et al., 2017). These studies include automated approaches to disassembling electronic scrap, as well as chemistry to extract REE from them. Recently Apple rolled out a Robot for iPhone dismantling which can dismantle up to 200 devices/hr. Processing 100,000 iPhones has the potential to yield 1900 kg of aluminum, 770 kg of cobalt, 710 kg of copper, 93 kg of tungsten, 42 kg of tin, 11 kg of REE, 7.5 kg of silver, 1.8 kg of tantalum, 0.97 kg of gold and 0.1 kg of palladium. The company reiterated its 2017 pledge to use only recycled materials in its supply chain (https://resource-recycling.com/e-scrap/2018/04/26/apple-rolls-out-robot-for-iphone-dismantling/).

REE separation chemistry is a big challenge and a chief barrier to possible widespread recycling activity, which is currently performed at a rate of only ~1%. Separation and purification of individual REE is challenging due to their chemical similarities. To develop other sources of REE and reduce the environmental impact of their isolation, there is a clear-cut need for new separation technologies that reduce the cost of industrial-scale REE separations and recycling. In this context, Fang et al. (2017) developed a simple, fast, and low-cost technology to help recycle mixtures of REE. Schelter's group has synthesized new organic compounds (a 'ligand'): tris (2-tert-butylhydroxylaminato) benzylamine (H_3TriNO_x) for separations. The central hypothesis of this work is that these tailored organic compounds can provide simple and effective separations for mixtures of REE, based on solubility differences of the REE complexes. The method developed by Schelter and his team is expected to contribute to reducing waste and reduce REE mining activity by adding recycled REE to the supply chain. U.S. Department of Energy's Critical Materials Institute (CMI) developed a method of using bacteria to produce acids to dissolve and separate REE from shredded electronics. Gluconobacter bacteria consumes sugars and produces acids and the method is more environmentally friendly (CMI, 2018). Further work is currently under way by these workers to develop the concepts into practical and industrially viable recycling processes. From the studies currently underway and the progress made so far, it is expected that the recycling of REE has the potential to be economical and more readily achievable than the exploitation of new mineral deposits.

10. R&D studies on the reducing their usage or on substitution for REE in different applications

Because of the environmental, cost and supply problems, lot of R & D studies have been initiated recently either to reduce the amount of REE usage in a particular application or to find out alternate and less harmful material for substitution for a particular REE. Machida et al. (2017) have designed a new autocatalyst that reduces the amount of Ce used by 30% from reference catalysts. The grafted cerium oxide, $CeO_2/MnFeO_y$, has both fast release and large storage capabilities for oxygen and has high performance capability for converting NO_x, CO, and total hydrocarbon to less harmful materials. Several countries have already started working on finding substitutes to REE devices. Hitachi Metals is working on a magnet that minimizes the use of REE by employing copper alloys. U.S. Department of Energy is funding many projects to look for substitutes of REE and to create REE-free devices. Toyota is developing future hybrid vehicles that do not require REE. Some groups are trying to develop a "super magnet" by layering of iron and nickel which is designed to be synthetic form of tetrataenite, a rare magnetic extra-terrestrial iron-nickel alloy found only in meteorites. This can be a future substitute for Nd. Fluorescent light bulbs

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and LEDs depend on phosphors made from Tb, Eu and Yb. Organic LEDs (OLEDs) and halogen incandescent lights are REE-free and can be used as substitute lighting. As markets shift to these alternatives, demand in those REE can decrease. Studies are also going on to create cheaper magnetic materials for cars and wind turbines (Pathak et al., 2015; Pavel et al., 2017). Lots of other leading multinational electronic firms such as Samsung are vigorously working on replacing REE in their applications. On the other hand, some technologists feel that REE are allowing the miniaturization of the components of high-tech-mass-produced-consumer-devices that transform electrical signals in to motion, sound, images and light, and it may be very difficult to replace them economically in the near future.

11. Chemical characterization of REE—Application of different instrumental analytical techniques

The chemical analysis of REE in geological, industrial and environmental materials is essential for geochemical exploration studies, mining, extraction, quality checks of both raw materials and finished products in industry, and also monitoring the environment. Physical and chemical similarities of REE make their determination usually difficult and complicated. This is particularly true if a selected element among them has to be determined in the mixture of the other REE, because of numerous interferences and coincidences. In the past accurate determination of REE in geological materials at their crustal abundance levels by using classical methods such as gravimetry, titrimetric, spectrophotometry, flame atomic absorption spectrometry (F-AAS) and graphite furnace atomic absorption spectrometry (GF-AAS) was extremely difficult and time consuming (Wengert et al., 1952; Onishi et al., 1962; Saxena, 1970; Andreev et al., 1974). These techniques are not considered here. But currently with the availability of sophisticated instrumental analytical techniques, these tasks have become relatively simpler. Among the instrumental methods available currently, instrumental neutron activation analysis (INAA) and ICP-MS including HR-ICP-MS are commonly used for REE determination in different kinds of materials because of their multi-element capability, high sensitivity wide linear dynamic range, fewer interferences, ease of operation and accuracy. In addition, techniques such as X-ray fluorescence spectrometry (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), glow discharge mass spectrometry (GD-MS), laser induced breakdown spectroscopy (LIBS) and recently introduced microwave plasma atomic emission spectrometry (MP-AES) are also found to be extremely valuable in such investigations. Though techniques such as isotope dilution thermal ionization mass spectrometry (ID-TIMS) and spark source mass spectrometry (SSMS) were used in the past for the determination of REE particularly in geological materials, currently their application is limited because of the requirement of tedious sample preparation methods and huge cost (Jochum et al., 1988; Klinkhammer et al., 1994). On the other hand, multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) is superior in terms of the analytical reproducibility compared with quadrupole ICP-MS or with ID-TIMS techniques for the determination of REE in geological materials. Precisions <0.4% can be obtained for all REE (Baker et al., 2002). Some of the important analytical techniques and their utility towards REE analysis in different applications are considered briefly in the following.

11.1. X-ray fluorescence spectrometry (both WD-XRF & ED-XRF)

X-ray fluorescence spectrometry (XRF) is a reliable method for trace element analyses at the μg/g level although the technique is relatively insensitive to the REE (Table 6). However, XRF, as a conventional analytical technique for REE analysis, has distinct advantages over the other methods in respect to its accuracy, speed and cost. Its only disadvantage is relatively low sensitivity. It can be classified into wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) and energy-dispersive X-ray fluorescence spectrometry (ED-XRF) according to the methods of excitation, dispersion, and detection (Potts and Webb, 1992). Both forms, namely, WD-XRF and ED-XRF techniques have been successfully applied for the determination of REE in geological and environmental materials. In general, because of higher detection limits offered by this technique for all REE, many determination methods involve separation and preconcentration procedures for their accurate determination (De Vito et al., 2000). For example, Juras et al. (1987) have developed a rapid and sensitive procedure for analyzing REE in geological samples, ranging in composition from ultramafic rocks to rhyolite by XRF after all REE are separated from other constituents by an ion-exchange procedure. Wu et al. (2010) have presented review on the applications XRF analysis in Chinese rare earth industry. The applications consisted of the analysis of REE in ores and soil, concentrates, compounds, metals, alloys, functional materials, fast and online analysis in separation process, and so on. Smoliński et al. (2016) have used WD-XRF to determine the content of 16 REE in several samples of combustion ash of coals from Polish mines. In recent times portable XRF (ED-XRF form) is being used successfully for on-site in the field quantification of REE including La, Ce, Pr, and Nd, as well as typical REE pathfinders in geochemical exploration studies including Y, Th, and Nb (Balaram, 2017). These gadgets are extremely valuable in the field as they help to quickly determine the next course of action in exploration, ore grade/process control and environmental sustainability studies.

11.2. Laser-induced breakdown spectroscopy (LIBS)

LIBS is an emission spectroscopic technique using a laser-generated plasma to ablate and excite the atoms in the sample, usually in solid form, although liquid samples can also be analyzed (Radziemski and Cremers, 2013; Balaram, 2017). Laser ablation of solids or liquids can directly fingerprint elemental constituents via their characteristic optical emission spectra. Detection limits can range from between 10 μg/g and 100 μg/g for most REE (Table 6) in common applications with precisions ranging from 3% to 5% and often better than 2% for homogeneous materials (Cremers and Radziemski, 2006). Both desktop and hand-held models are available from different firms. LIBS technique has numerous advantages compared to other techniques, as it allows very fast measurements, can be employed in the field, requires no sample preparation, and consumes only tiny amounts of sample. The greatest advantage of LIBS is its ability to do real time identification of different metals including REE and also non-metals in seconds (Bhatt et al., 2018). This feature will be of special use in recycling operations and recovery of REE components from scrap electronics. The accuracy of solid measurements using LIBS is often compared to that of XRF, which can also measure elements in solid targets on site. Considering the overall accuracy, it can be said that the suitability of LIBS for in-situ analysis is comparable to XRF (Takahashi and Thornton, 2017).

11.3. Instrumental neutron activation analysis (INAA)

INAA is a high-sensitive and versatile analytical technique for the determination of the concentration of major, minor and trace elements in a variety of matrices. A small sample of 5 to 100 mg is subjected to a neutron flux in a nuclear reactor. The stable nuclei absorb neutrons and become unstable radioactive nuclides and the

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resultant radioactive nuclides decay with emission of particles or, more importantly gamma rays, which are characteristic of the elements from which they were emitted. The energy of the emitted gamma rays is used to identify the nuclide and the intensity of the radiation can be used to determine its abundance. Semiconductor radiation detectors are normally used for quantitative measurement. Comparison of the intensity of these gamma rays with those emitted by a standard, permit a quantitative measure of the concentrations of the various nuclides. This technique is extremely popular because nuclear reactions and decay processes are virtually unaffected by chemical and physical structure of the material during and after irradiation. Several workers have applied INAA technique for the determination of REE at extremely low concentrations in different earth and environmental samples (Vukotić, 1983; Baidya et al., 1999; Bounouira et al., 2007; Alharbi and El-Taher, 2016). Ravisankar et al. (2006) have determined REE in beach sands from Tamil Nadu, India by INAA to understand their geochemical behavior. Table 7 presents the REE results of the Ocean bed polymetallic nodule reference sample (2388) from Indian Ocean (Pandey, 1992) determined by INAA in comparison with the data obtained by the author using other popular analytical techniques, namely ICP-MS and ICP time-of-flight MS (ICP-TOF-MS). As certified data for several elements including REE are not available for this unique Indian reference material, this data will be valuable for providing certified values for all REE in future. Though INAA is a sensitive and multielement technique, it has certain limitations. For more precise determinations, INAA needs matrix matching reference materials for calibration to allow for the emitted X-rays which are subjected to self-attenuation in the sample under the same counting conditions. Hence synthetic standards prepared by mixtures of REE are not suitable unless the matrix is also matching to that of the sample. Table 8 presents concentrations (μg/g) of REE obtained by INAA in ferromanganese crust (cobalt crust) samples crust samples collected from the Afanasy Niktin Seamount (ANS) in the Eastern Equatorial Indian Ocean, using the procedure described by Figuelredo and Marques (1989). Calibrations were performed using international polymetallic nodule reference samples, Nod-A-1 and Nod-P-1. INAA is very sensitive technique and is therefore extremely valuable for the determination of REE in geological and environmental materials. Despite these advantages, INAA is certainly not a popular analytical technique as it is time-consuming, not independent, requires a reactor nearby and involves longer cooling times for certain elements.

Table 7
Comparative concentrations (μg/g) of REE in the Indian Polymetallic Nodule Reference Material, 2388 by INAA, ICP-MS and ICP-TOF-MS.

Elements	INAA	ICP-OES	ICP-MS	ICP-TOF-MS
La	194 ± 4	223.27	187.70	203.31
Ce	798 ± 24	851.68	806.70	841.26
PGR	-	-	45.12	58.35
Nd	144 ± 5	243.60	182.40	212.00
Sm	45.0 ± 0.9	-	43.80	48.48
Eu	12.4 ± 0.4	13.32	10.43	9.99
Gd	-	43.65	44.52	45.22
Tb	7.9 ± 1.1	7.26	7.42	8.18
Dy	-	-	40.20	42.32
Ho	-	-	7.31	7.80
Er	-	22.10	19.81	18.61
Tm	-	-	2.91	2.95
Yb	16.0 ± 1.3	18.7	17.85	17.60
Lu	2.1 ± 0.2	3.75	3.13	2.96
Y	-	113.10	107.1	133.83
Sc	10.6 ± 0.5	9.80	11.1	-

INAA: This study was measured at the Institute of Energetic and Nuclear Research, Sao Paulo, Brazil; ICP-OES*: direct, without separation or preconcentration (Balaram et al., 1995); ICP-MS: Balaram et al. (1995); ICP-TOF-MS: Balaram et al (2013a, b).

Table 8
Concentrations (μg/g) of REE in ferromanganese crust (cobalt crust) samples collected from the Afanasy Niktin Seamount (ANS) in the Eastern Equatorial Indian Ocean.

Elements	CC2-ADR24 Ferro manganese crust	CC2-ADR25 Ferro manganese crust	CC1-DR-12 Ferro manganese crust
La	217 ± 3	189 ± 3	236 ± 5
Ce	1163 ± 34	1186 ± 35	1041 ± 31
Nd	232 ± 8	122 ± 5	185 ± 6
Sm	35.4 ± 0.7	27.0 ± 0.5	39.0 ± 0.8
Eu	8.5 ± 0.3	6.4 ± 0.2	9.2 ± 0.2
Tb	6.8 ± 0.8	4.7 ± 0.6	6.5 ± 0.7
Yb	17.3 ± 1.5	15.5 ± 1.3	19 ± 2
Lu	2.4 ± 0.2	2.1 ± 0.2	2.5 ± 0.2
Sc	8.8 ± 0.4	9.0 ± 0.4	11.0 ± 0.5

Note: The samples were determined by NAA facility by the author at the Institute of Energetic and Nuclear Research, Sao Paulo, Brazil.

11.4. Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES is a multi-element analytical technique used for the accurate determination of different elements at major, minor and trace concentration levels in a variety of materials. A liquid sample is converted to an aerosol and transported to the high temperature inductively coupled plasma. In the plasma the sample undergoes desolvation, vaporization, atomization and ionization. The atoms and ions then absorb energy from the plasma which causes electrons within them to move from one energy level to another. When the electrons fall back to ground state, light of wavelengths specific to each element are emitted. The measured emission intensities are then compared to the intensities of reference materials of known concentrations to obtain the respective elemental concentrations in an unknown sample (Greenfield et al., 1964; Wendt and Fassel, 1965). The technique can simultaneously measure up to 60 elements with high sensitivity and an extraordinarily wide linear dynamic range which is perhaps the most outstanding feature of the ICP-OES (Balaram et al., 1995). Bentlin and Pozebon (2010) determined low concentrations of the fourteen naturally occurring lanthanides directly by ICP-OES after selecting the most appropriate spectral lines. But in general, due to several spectral interferences encountered during the determination of REE in geological materials, it is essential to adopt a separation and preconcentration procedure before their determination by ICP-OES. Jarvis (1994) determined REE and Y in 37 international rock reference materials by ICP-OES after adopting a cationic-exchange chromatography for their separation and preconcentration followed by a conventional rock dissolution technique. It's very challenging to accurately determine REE and other trace elements in the presence of large concentrations of REE in a sample, using ICP-OES because the line-rich spectra emitted by REE. Chausseau et al. (2014) have obtained very high-quality results on the analysis of cerium oxide, gadolinium oxide and NdFeB magnetic materials matrices using high resolution ICP-OES. In general, because of the spectral complexities and relatively low concentrations of REE in different types of rocks, separation of the REE via ion exchange is required after sample digestion prior to analysis by ICP-OES making this technique less productive (Walsh et al., 1981; Jarvis and Jarvis, 1985; Balaram et al., 1995). Clarice et al. (2017) have determined REE in geological and agricultural materials using ICP-OES by measuring the emission signals in radial as well as dual viewing modes for obtaining information geochemical formation history, plant nutrition status, need for supplementation and possible contamination.

11.5. Microwave plasma atomic emission spectrometry (MP-AES)

A new commercial instrument representing yet another analytical technique called the MP-AES has been introduced in 2011, which appeared to provide an attractive alternative to ICP-OES for REE determinations. The MP-AES system utilizes a relatively new design of plasma torch, utilizing nitrogen gas for generating high temperature microwave plasma as reported by Hammer (2008). With the detection limits for many REE in μg/g range (Table 6), the utility of MP-AES has been demonstrated using several different geological and environmental matrices, including industrial effluents, water, sediments, soils, rocks and ores during the last 5 years (Balaram et al., 2013a, 2014; Kamala et al., 2014; Sreenivasulu et al., 2017). Helmeczi et al. (2016) developed a novel methodology for rapid digestion of REE ores and determined REE both by MP-AES and dynamic reaction cell-ICP-MS. The REE results obtained by MP-AES were identical to those obtained by ICP-MS. Tupaz et al. (2015) determined scandium in a laterite sample using MP-AES and the results favorably compare with those obtained by ICP-MS. Currently MP-AES is a potential analytical technique for inorganic contents in a variety of geological and environmental materials, because it has a number of obvious advantages over techniques such as F-AAS and ICP-OES. Given the similarity of sample introduction systems between the MP-AES and conventional ICP-OES, it is anticipated that sample introduction and sample preconcentration strategies already validated for ICP-OES will be equally robust for MP-AES, which would make MP-AES an attractive alternative technique in future as it is cheaper.

11.6. Inductively coupled plasma mass spectrometry (all forms of ICP-MS, ICP-TOF-MS, HR-ICP-MS & MC-ICP-MS)

ICP-MS occupies an invaluable position in the modern analytical laboratory due to its simplicity, excellent sensitivity, very limited interferences, precision and accuracy (Balaram, 1995). In the past, until time of the advent of ICP-MS, the determination of REE in geological samples was a difficult and expensive task involving separation of the REE by utilizing time consuming methods such as precipitation, solvent extraction and ion exchange prior to analysis by techniques such as XRF and ICP-OES. Even INAA method of determination of REE was also very slow because of sample irradiation and cooling requirements. But the successful linking of ICP to the quadrupole mass spectrometer has presented the analyst with a most valuable addition to the range of techniques available for elemental analysis (Houk et al., 1980). The ICP source converts the atoms of the elements in the sample to ions. Samples, usually in solution form reach the plasma as aerosol after passing through a nebulizer and a spray chamber/desolvator. In addition to the solution nebulization, different other sample introduction systems such as laser ablation and different chromatography techniques can be coupled to the instrument allowing direct analysis of solids and speciation analysis capability. At the high temperature attained in the plasma source, most elements including those with higher ionization potentials can be almost completely atomized and ionized. A portion of the ions generated are then separated and detected by the mass spectrometer and analyzed on the basis of m/z ratios. Over the last 35 years, ICP-MS has been well established as a powerful analytical tool for rapid multielement analysis. Extremely low detection limits (Table 6), high sample throughput, requirement of very small quantities, element versatility (major, minor, trace and ultra-trace) and isotopic detection capability are some of the very important features that have made ICP-MS an excellent analytical technique for the analysis of a variety of materials (Balaram et al., 1995). Several workers world over including from our laboratory have determined REE in different types of materials using ICP-MS during the last three decades or so (Date and Gray, 1985; Jarvis and Jarvis, 1985; Lichte et al., 1987; Balaram, 1996; Dey et al., 2018). Isotope dilution ICP-MS can provide highly precise REE data in different materials including geological materials (Tanaka et al., 2018). Currently ICP-MS (including HR-ICP-MS) technique is being very extensively applied for the accurate determination of REE in different types of materials (Fig. 5) when compared to other popular analytical techniques such as INAA, ICP-OES, XRF and UV-vis spectrophotometer. Table 9 presents a comparison of concentrations of REE (μg/g) in USGS manganese nodule reference materials, Nod-A-1 and Nod-P-1by different popular instrumental analytical techniques including ICP-MS (Nath et al., 1992).

Development of ICP-TOF-MS brought yet another dimension to the trace analysis in recent times (Mayers and Hieftje, 1993; Mahoney et al., 1997; Balaram et al., 2013b). ICP-TOF-MS offers extremely high data-acquisition speeds, high ion transmission and quasi-simultaneous measurement of all masses in packet extracted from the ion source leading to better detection limits than those offered by quadrupole ICP-MS (Table 6). Table 7 presents REE data (μg/g) in the Indian Polymetallic Nodule Reference Material, 2388 obtained by ICP-TOF-MS in comparison with the data by other analytical techniques, namely, INAA and ICP-MS.

Out of different forms of ICP-MS, HR-ICP-MS has gained confidence especially by the scientific community in recent years due to its extremely high sensitivity and capability to clearly resolve several spectroscopic interferences. HR-ICP-MS combines an ICP source with a double focusing magnetic analyzer to perform trace/ultra-trace metal analysis and/or isotope ratio measurement (Balaram, 2018; Singh et al., 2018; Satyanarayanan et al., 2018a). This instrument can be utilized in high resolution mode to resolve even most complex interferences (Bradshaw et al., 1989) or even at lower resolution to provide extremely low detection limits. Current HR-ICP-MS instruments have resolving powers up to 10,000 and will be typically operated at preset resolution settings for low, medium or high (Walder and Freedman, 1992; Satyanarayanan et al., 2018b). This is the most sensitive analytical technique available today for inorganic analysis. This is evident from the results in Table 6 where the detection limits of REE obtainable by HR-ICP-MS are presented in comparison with some contemporary popular instrumental analytical techniques. Table 6 also shows maximum permissible REE concentrations in drinking water published by Sneller et al. (2000).

Multi-collector ICP-MS (MC-ICP-MS) system combines a plasma source (ICP), an energy filter, a magnetic sector analyzer, and multiple collectors for the simultaneous measurement of different isotopes. This powerful technique measures precise isotopic ratios

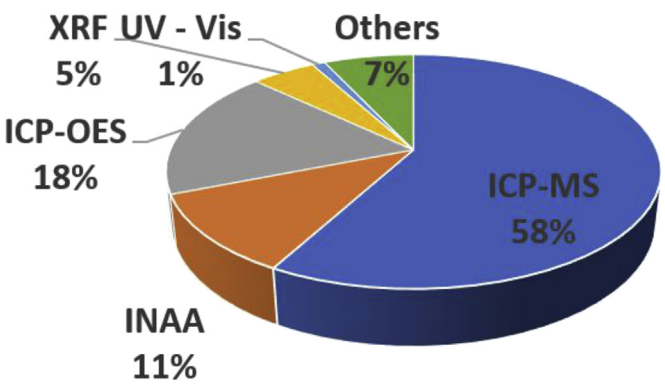


Figure 5. The application of different analytical techniques for REE determination in the earth and environmental materials (ICP-MS includes HR-ICP-MS also).

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Table 9
Comparison of concentrations of REE (μg/g) in USGS manganese nodule reference materials, Nod-A-1 and Nod-P-1 by different popular instrumental analytical techniques.

Elements	Nod-A-1 (collected from Atlantic Ocean)				Nod-P-1 (collected from Pacific Ocean)				
	ICP-MS	ICP-OES	INAA	SSMS	ICP-MS	ICP-OES	ICP-OES	INAA	SSMS
La	115	112	133	130	105	103	107	120	82
Ce	656	676	668	>300	318	288	296	289	280
Pr	21.7	-	-	23.0	27.5	-	-	-	27.0
Nd	94	105	85.3	94	114	135	143	113	110
Sm	20.4	24.7	20.9	21.0	27.2	33.8	35.3	30.4	28.0
Eu	5.81	6.10	4.48	4.80	7.44	7.75	9.04	6.57	6.80
Gd	34.3	23.6	26.5	22.0	33.8	27.0	32.5	29.4	24.0
Tb	4.20	-	-	3.80	4.53	-	-	-	4.20
Dy	25.80	22.40	-	22.0	25.99	29.20	27.00	-	25.00
Ho	5.09	4.70	-	5.30	4.73	5.13	4.93	-	5.10
Er	15.6	14.4	-	15.0	13.3	15.2	13.4	-	13.0
Tm	2.19	-	-	-	1.72	-	-	-	-
Yb	15.40	11.80	16.30	13.50	13.26	12.30	11.50	13.8	13.00
Lu	2.21	1.92	2.16	-	1.75	1.89	1.66	1.85	-

ICP-MS: Nath et al., 1992; ICP-OES: Ingri and Ponter (1987); INAA: Flanagan and Gottfried (1980); SSMS: Rankin and Glasby (1979).

of number of isotopes simultaneously which has enabled significant advances in our understanding of geological, biological, nuclear, and physical processes in terrestrial and extra-terrestrial environments (Balaram, 2018). This technique is probably the best technique at present for the precise determination of REE and isotope ratios. Although isotope dilution using thermal ionization mass spectrometry (TIMS) is the best technique for discriminating and stabilizing the ion beams among REE (e.g. Masuda et al., 1973), the technique requires robust laboratory methods. MC-ICP-MS can provide highly reproducible data (<0.2%) for all REE in geological materials very rapidly (Baker et al., 2002). Extremely accurate and precise REE data, with analytical uncertainty typically >1% can be obtained using isotope dilution MC-ICP-MS (Kent et al., 2004).

11.7. Glow discharge mass spectrometry

Like most mass spectrometric techniques, glow discharge mass spectrometry (GD-MS) has also become an established analytical tool for the analysis of major, minor, trace and ultra-trace compositions over a wide dynamic range (ng/g to 100%), in solid materials including geological metallurgical and semiconductor materials (both conducting and non-conducting) with a range of applications spanning several disciplines (King et al., 1995; Becker and Dietze, 2003). The first commercial GD-MS, magnetic sector model VG 9000 ("Thermo Elemental", Winsford, UK) was built in 1985. Taking the detection limits for various REE to sub-μg/g levels (Table 6), this technique is valuable in checking the purity levels of individual rare earth oxides.

11.8. In-situ analytical techniques for REE

The micro-analysis of elemental concentrations direct in solid samples has been an attractive frontier in the development of analytical science. Gray (1985) was the first to demonstrate the feasibility of analyzing direct solids by ICP-MS using laser ablation sampling (LA-ICP-MS). Compared with solution nebulization-ICP-MS for the bulk analysis of geological samples, LA-ICP-MS analysis has several advantages such as very low background, lower oxide and hydroxide interference levels, a simpler sample preparation procedure, faster analyses, and cost effectiveness. For example, the same fusion beads prepared for XRF analysis can be used for the determination of major, minor and some selected trace elements including REE by LA-ICP-MS. John et al. (1993) developed a rapid method for the analysis of REE and several other trace-elements on direct whole-rock fused glasses using laser sampling ICP-MS. All REE including Y and Sc can be measured at sub-μg/g levels (Table 6). In a study, Tanaka et al. (2007) determined REE concentrations in carbonate samples using LA-ICP-MS. The effect of matrix on LA-ICP-MS analysis was investigated using NIST glasses and synthetic $CaCO_3$ doped with REE as calibration standards. The influence of the matrix on LA-ICP-MS analysis was found to be relatively small. Liu et al. (2013) have presented an excellent review of the application of LA-ICP-MS for the analysis of geological samples for major, minor and several trace elements including REE. Secondary ion mass spectrometry (SIMS) or Ion-Microprobe is one of the best techniques for the analysis of REE in geological materials (Sano et al., 1999). SIMS relies on the physical phenomenon of "sputtering" to produce analyte ions. A primary beam of ions (generally O^+ or Cs^+) is accelerated into a solid sample at potentials of a few kV. The impact of these primary ions gradually erodes ("sputters") a shallow crater in the sample. A portion of the material sputtered from the sample emerges as ions, and these "secondary" ions are the analyte species that are introduced into the mass spectrometer for subsequent detection and quantification (Muir et al., 1987). These instruments are capable of both isotopic ratio analysis and sub-μg/g elemental analysis with extremely high spatial resolution. The spatial resolution of SIMS is better (5–10 mm) than that of LA-ICP-MS, which is typically >10 mm. However, SIMS is a less rapid and more complex analytical technique than LA-ICP-MS. Highly sophisticated similar analytical tool, sensitive high-resolution ion micro probe (SHRIMP) with special resolution ~ 25 μm, which mostly applied for the determination of high precise isotopic ratios, is also used to determine REE distributions in fly ash glasses to test the REE partition into the glass, in studies related to the extraction of REE from coal ash (Ireland et al., 2008; Kolkerer et al., 2017).

12. Conclusions

Fast emerging green technologies ranging from electric car batteries to solar panels to wind turbines, in addition to others where REE are widely being used together with price rise, are expected to drive tremendous growth and demand for these metals in near future. There is a greater need to intensify our search for REE resources not only on land but also in ocean bottom sediments. Deep sea mining would definitely be a feasible option in near future in addition to the development of cost-effective recovery of REE from abundant coal, coal ash and red mud. There is a great need for developing a sustainable exploitation schemes for all kinds of REE ore deposits and meticulously follow to prevent further damage to the environment as it will take a long time and cost a great deal of money to restore the environment and to ensure the sustainable development of the REE industry. Instead of opening new mining ventures, extraction of REE from coal fired ash, red-mud and electronic recycling schemes are considered promising options for near future REE supply. The wide-spread application of REE in different industries as well as agriculture is alarmingly increasing leading to a constant increase of the concentrations of these elements in the environment which would not only disturb the aquatic system but also the plant and soil ecosystem leading to number of human health issues. Close monitoring may be needed at places where phosphate-based fertilizers are used, and in areas where soil conditions are favorable to REE mobility, availability and uptake by plants, and/or at e-waste dump sites where surface runoff could contaminate the local environment. Extensive utilization of REE in day-to-day life may warrant an urgent toxicological assessment of these elements from a human health perspective. Recycling of REE

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from e-waste has not yet taken off and more emphasis should be put on the R & D efforts on finding out substitutes for REE to draw away from reliance on REE. Though several studies have been initiated to find out good substitutes for REE in different technologies, so far there is no breakthrough in any of the critical technologies, and more studies are required. The innovative processes and designs are needed to be developed for REE extraction and process from different sources which also must adequately address the environmental safety and human health issues. In all these activities, precise and accurate determination of individual REE in different materials both in solid and liquid forms becomes essential. Currently an array of high-sensitive and selective analytical techniques is available for the accurate and precise determination of REE in different materials. Performance characteristics such as multielement nature, high sensitivity and high resolving power of most interferences, HR-ICP-MS would certainly become an important analytical tool in REE activities in future.

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