Geological Perspectives of Rare Earth Elements in India with a Special Reference to Tamilnadu: A Review

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Abstract: Rare Earth Elements (REEs) are a set of 17 elements belonging to lanthanide group, Yttrium and Scandium. These are used in a wide spectrum of hi-tech applications in industries like electronics, green energy, communications, defense, automobiles etc., World-over, these elements occur in the earth in different geological environments like alkaline rocks and carbonate rocks of igneous origin called carbonatites, residual deposits resulted from weathering, heavy mineral sand placers, coal and continental shelf and ocean bottom sediments. In India, REEs occur mainly in carbonatites, alkaline rocks, beach sand placers and weathering product of ytrrium rich xenotime minerals. In Tamilnadu, alkaline rocks occurring mainly in Dharmapuri shear zone and beach placer sands developed in coastal districts are found to be rich in REE.

Key words: REE, carbonatites, beach placer sands, xenotime

1 Introduction

Rare Earth Elements (REEs) include a set of 17 elements collectively called as Lanthanides - the elements with atomic numbers 57 to 71 (15 elements) and Scandium and Yttrium. The term REE was derived from uncommon mineral gadolinite

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found in village Ytterby, Sweden which was a source of these elements. However, except the unstable promethium, other REEs occur in higher concentration in the earth. For eg. the general content of one of REEs - Cerium being 62ppm ranking 25th most abundant element in the earth. The REEs occur in the decreasing order of abundance in the earth's crust as Ce⁵⁸-62 ppm, Nd⁶⁰-33ppm, La⁵⁷-32ppm, Y³⁹-29ppm, Sc²¹-22ppm, Pr⁵⁹- 9ppm, Sm⁶²-7ppm, Gd⁶⁴- 6ppm, Dy⁶⁶-6ppm, Er^{68} -3.03ppm, Yb^{70} -2.93ppm, Eu^{63} -1.8ppm, Ho^{67} -1.17ppm, Tb^{65} -0.94ppm, Tm^{69} -0.47ppm, Lu⁷¹-0.46ppm, Pm⁶¹-infinitesimal (UNCTAD, 2014). The REEs do not occur separately but together in different concentrations. It is divided in two groups namely Light REE (La⁵⁷ to Eu⁶³) and HREE (Gd⁶⁴ to Lu⁷¹). LREE and HREE proportions vary in minerals. The common REE minerals Bastnaesite, Monazite and Xenotime have different concentrations of LREE and HREE. Monazite is reported to contain more HREE than Bastnaesite. The largest source of HREE is said to be Xenotime with concentration of Dysprosium, Erbium, Holmium, Ytterbium and Yttrium. Since REEs have wide utility in advanced fields of electronics, communication, defense, industry especially green technology etc., there are growing interests by technology developers as well as exploration geologists.

2 Hi-tech applications of REE

REEs have wide variety of applications in emerging hi-tech areas. They are useful in electronics-PCs, mobile phones, silicon chips, rechargeable batteries, LEDs, fluorescent lamps etc.,; in technology - lasers, masers, radar detection devices, superconductors, fiber optics, computer memory.,; in manufacturing - high strength magnets, metal alloys, chemical oxidizing agents, strengthening other metals, automotive catalytic converters etc.,; in medical sciences - portable X-ray machines, MRI contrast agents, nuclear medicine imaging, cancer treatment applications, etc.,; renewable energy - hybrid automobiles, wind turbines, biofuel catalysts, etc., By virtue of being useful in many hi-tech fields, they are also called as 'vitamins of modern Industry' (Balaram, 2019). As these elements have multiple utilities, their uses are likely to increase exponentially in future.

3 Geological environs of REE minerals

Many geological processes result in the formation of REE deposits. REE minerals are diverse and complex. About 245 REE minerals are known to be occurring as carbonates, oxides, silicates and phosphates. In general, REEs are found in nature mainly in four geological environments namely carbonatites, alkaline igneous complexes, ion-adsorption clay and monazite -xenotime placer deposits (Balaram, 2019).

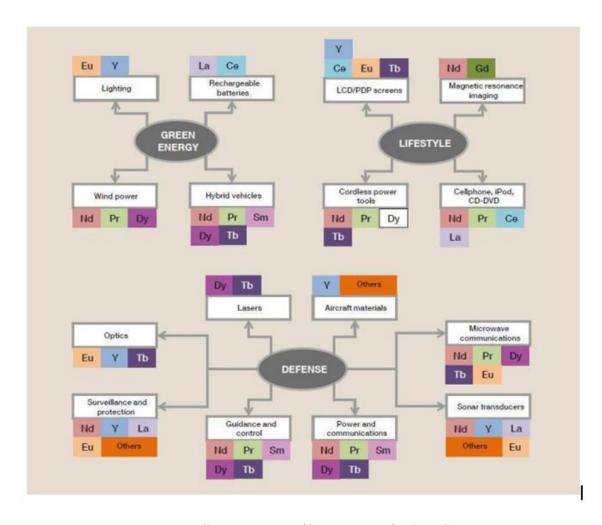


Figure 1: REEs uses in different sectors (Source: UNCTAD, Special issue on Rare Earths, 2014 fig.6)

Carbonatite magmas are resulted from mantle derived primary carbonate rich melts or by evolution from mantle related alkali melt by fractional crystallization. As crystallisation progresses in this carbonatite magma, REEs can be concentrated as the primary REE mineral phase or they can be enriched in the late stage melt. Peralkaline magmas are another important source of REEs. Alkaline rocks crystallise from silicate magmas rich in alkali elements and K- and Na- rich elements precipitate from these magmas. These peralkaline magmas are found to be enriched in REEs. Another significant source of REEs is the ion adsorption clay deposits in south China. REEs are concentrated in the clay by the leaching from the underlying granites by groundwater, intense weathering of the REE rich granites, ion adsorption of mobilized REE onto the clay. REE rich monazite and xenotime called heavy minerals are also concentrated in the inland and beach placers. In both these

deposits, heavy minerals are physically sorted and deposited by the action of gravity and water flow. The heavy minerals comprise of minerals heavier than common silicate minerals namely quartz (s.g.2.65) and felspars (s.g.2.54 to 2.76) and include the minerals with specific gravities more than 2.8 to 2.9. Inpractice, the minerals which sink in the bromoform liquid medium (s.g.~2.89) are called as heavy minerals.

4 World REE deposits scenario

The total world reserve of Rare earth oxides (REO) is reported to be about 120 million tons in which China accounts for about 36% while Vietnam and Brazil contribute 18% each followed by Russia 15% and India (6%) (IBM, 2018). Presently, China is the world leader in exploration and also production. In China, important production centers are reported to lie at Baotou, Inner Mongolia and Jiangxi and Sichuan provinces. In Sichuan and Gansu areas, REEs occurs as Bastnaesite and it is recovered as a biproduct from iron ores at Baotou area. Yttrium is reported to be produced from ion adsorption clays in Jiangxi, Guangdong, Hunan and Jiangsu provinces. In Russia, loparite, titanium-tantalum niobate mineral is obtained from Lovozero massif in the Murmansk region. Byproducts from titanium bearing minerals are the source of REE in Australia and obtained from Tin dredging in Malaysia (IBM, 2018). In 2010, there was surge in exploration for REE world over following rare earth crisis after the China's monopoly in the REE market. Status and listing of about 260 REE deposits spread over the globe with their grades, tonnage and details of selected deposits was detailed by Weng et al., 2015.

5 Geological environment of REE deposits in India

Carbonatites: Carbonatites of India are broadly divided into two groups based on age and type of surrounding rocks as volcanic rocks complexes of Cretaceous age and plutonic rock complexes of proterozoic age. The carbonatites of subvolcanic to volcanic rock complexes include Amba Dongar, Siriwasan-Nakal and Hingoria areas in Baroda dt of Gujrath; Mer-Mundwara in Sirohi dt and Sarnu-Dandali-Kamthai in Balmer dt of Rajasthan; Swangre-Jasra, W. Khasi Hills dt of Megalaya; Chhaktalo in Jabua dt of Madhya Pradesh; Mahdawa, Dhulia dt of Maharashtra. Carbonatites of plutonic complexes include Newania, Udaipur dt of Rajasthan; Sevathur, Samalpatti, Pakkanadu-Mulakadu, Hogenakal in Dharmapuri dt, Udaiyapatti-Chinnagoundanpalayam in Salem dt of Tamilnadu; Ajjipura-Kollegal, Mysore dt, Karnataka; Sung Valley, Jaintia Hills dt of Megalaya; Samchampi in Karbi-Anglong dt of Assam; Beldih in Purulia dt of W.Bengal. Minor

veins of carbonatite in syenite, nephline syenite, alkali granite complex including Elchuru in Prakasam dt, Kunavaram in Khammam dt of Andhra Pradesh; Munnar of Kerala; Khambamettu in Madurai dt of Tamilnadu are also included in plutonic group. The other important type of carbonatite Kimberlite- Lamproite association includes Khaderpet in Cuddapah dt of Andhra Pradesh; Chitrangi region of Utter Pradesh; Pachcham Islands in N.Kutch of Gujarath, Ariyalur in Trichy dt of Tamilnadu; Murud-Janjira in Ratnagiri dt of Maharashtra (Krishanamurthy, 2019). Important geological environments of REEs are shown in the schematic figure. Petrologically, they are associated with carbonatite-nephelinite-phonolite (Amba Dongar, Gujarath), dunite-peridotite-pyroxenite-ijolite- melilitite (Sung valley, Mehalaya) and miaskitic syenite-pyroxenite \pm dunite (Sevathur, Tamilnadu). Genetically carbonatites can be grouped into direct partial melting from mantle (Newania, Rajasthan); liquid immiscibility from nephelinite associations (Newania, Rajasthan); fractionation of ultra alkaline, ultramafic and mafic associations (Sung valley, Mehalaya)(Krishna murthy, 2019).

Major Carbonatites hosting REE in India is in Amba Donger, Chhota Udepur District, Gujarat. Amba Dongar carbonatites is reported to host about in 105 million tons with 3% REO (Singer, 1998). Similarly, based on the geological studies REE rich carbonatite was identified at Kamthai, Barmer district, Rajasthan with a maximum total LREE of 17.31% and a weighted average of 2.97%. The carbonatite plug cover is reported to host about 4.91 million tons upto a depth of 84m making it one of world class deposit. REE minerals identified are bastanaesite, synchysite, carbocernaite, cerianite, ancylite and parisite (Bhushan and Kumar, 2013).

6 Placer beach sand deposits

Economically useful mineral concentrations are generally found in the placer beach sand deposits. REE minerals derived from granitic source or high grade metamorphic rocks are concentrated in the tertiary/Quarternary aged beach sand deposits. In India, monazite is reported to be the main source of REE (IBM, 2018;Balaram, 2019). Monazite bearing beach sand placer deposits with other economic minerals are reported to occur in the states of Kerala, Tamilnadu, Andhra Pradesh, Odisha (Krishnamurthy, 2020).

7 HREE areas in India

Peralkaline rocks and alluvial placers are opined to be enriched in HREE than carbonatites (Krishnamurthy, 2020). Neoproterozoic (745 \pm 10 Ma by Bhushan, 2000) aged volcanic-plutonic bimodal Siwana Ring Complex of Malani Igneous Suite of rocks of Rajasthan is reported to be enriched in HREE. REE minerals reported

include bastnaesite, parisite, La-Ce-Ba cebaite etc., HREE minerals content is reported to vary from 2.04 to 2.5% (Bhushan and Somani, 2019).

8 Yttrium rich geological environments in India

Yttrium rich xenotime placers are mainly reported in Central India. They are distributed in Deo and Pojenga rivers, Gumla dt of Jharkhand and Siri River, Jashpur dt of Chhattisgarh besides minor occurrences in other areas. Residual concentration from weathering rocks were found in gravels of Kanyaluka area, Singhbhum area, Jharkhand(Krishnamurthy, 2020).

Nonconventional Sources like coal fly ash from thermal power plants; tailing products after recovery of desired metal from Pb, Zn, Cu, Al and phosphate ores; metallugical slags of tin and steel plants were suggested to be potential for REE concentration (Rai, 2016).

9 REE scenario in Tamilnadu

Dharmapuri shear/rift zone extends over more than 200km x 50km wide zone from Bhavani in SSW to Gudiyattam in the NNE. Structures namely Mettur-Palakadu lineament in the west and Javadi Hills west lineament in the east bound this shear zone. Neoproterozoic alkaline magmatism is known in this shear zone. Alkaline - carbonatite plutons namely Pikkili, Hogenakkal, Pakkanadu, Kamaneri, Chalk hills, Samalpatti, Sundamalai, Sevathur, Elagiri, Rasimalai, Paravaimalai and are found to occur close to this shear zone (Renjith et al., 2016). The carbonatite complexes of Koratti, Samalpatti and Pakkanadu were reported to contain REE minerals (Semenov et al., 1978). The syenite dominated carbonatites of Tamilnadu with barite veins around Elagiri Alangayam was reported to be REE rich broadly comparable to Mountain Pass, California, USA (Krishnamurthy, 2020). Beach sand placer deposits of Tamilnadu containing titanium and non-titanium minerals occur along the coast of Tamilnadu. These titanium bearing minerals including Ilmenite, Rutile, Leucoxene and nontitanium minerals including Zircon, Monazite, Garnet, Sillimanite etc., are found in these beach sands are found in Thoothukudi, Kanniyakumari, Tirunelveli, Ramanathapuram, Pudukottai, Tiruchirapalli, Thanjavur, Cuddalur and Kanchipuram districts in the eastern coast of Tamilnadu (tnmines.tn.gov.in/mineral-wealth.php).

10 REE industry in India

Indian Rare Earths Limited (IREL), a Government of India undertaking and Kerala Minerals & Metals Limited (KMML), a Kerala State Government undertaking are reported to be engaged in mining and processing of beach sand minerals from placers deposits (IBM, 2018). REE is separated from monazite mined from Manavalakurichi, Kanyakumari district and chemically treated in the IREL processing plant at Aluva, Ernakulam district. Monazite is reported to be digested with caustic soda lye to produce trisodium phosphate and slurry which is used for the separation of diverse rare earth compounds. Individual rare earth oxides are separated out by solvent extraction and ion exchange facilities. India is reported be the second largest supplier of Yttrium In the world (IBM, 2018).

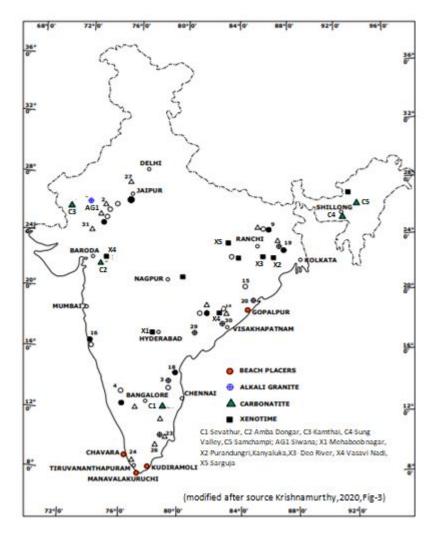


Fig.2: Sketch map showing interesting provinces of REE in India

11 Challenges in REE industry

Profuse use of REEs in multiple spectrum of applications in our modern life has a toll also. Indiscriminate dumping of e-waste is facilitating mixing of these elements into subsoil and groundwater. Gd which is used as contrasting agent in magnetic resonance imaging (MRI) is reported to pass through human body into environment. Trace elements finding their way into soil and waters may have their contribution in environmental pollution and human health. These health hazards can be minimized by the studies of identifying anthropogenic sources, mechanism of transfer, bioaccumulation and their environmental behaviour and by adoption of necessary public policies and development of effective treatment technologies (Balaram, 2019).

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