

## The need to explore for rare earth minerals

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*Rare earth elements (REEs) are strategic metals with critical applications in modern technology, and with no satisfactory substitutes. REE minerals do not occur concentrated in geological environments unlike those of base metals or iron ores and their geological exploration is often a daunting task. Mining, beneficiation and metallurgy of REEs constitute a complex process with adverse environmental impacts. The world REE market today is controlled by the Peoples Republic of China, which is moving ahead to impose a total export embargo on these metals by the year 2012. As a consequence, the entire world is vigorously exploring for REE minerals in an effort to counter China's threat. There are many favourable geological milieus in our country for REE mineralization which should be targeted for exploration.*

The rare earth elements (REEs) or lanthanides include 15 elements of the periodic table with atomic number,  $Z = 57-71$  (ref. 1). They are, in order of increasing atomic number, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Scandium (Sc,  $Z = 21$ ) and yttrium (Y,  $Z = 39$ ) are not REEs, but have chemical and physical properties identical to the REEs and are thus generally grouped under REEs. They are all metallic elements closely related to each other in their chemical properties, geochemical coherence and distribution in the earth's crust. Minor amounts of Th and U always occur associated with the REE minerals.

Apart from their use in petrogenetic interpretation, the REEs are high-tech metals with seemingly endless applications in modern electronic industry: they are used in mobile phones, defence hardware, LCD screens, computers, hard disks, energy-saving fluorescent lamps, MRI, positron emission tomography (PET), portable X-ray units, fibre optics, lasers, petroleum refining, glass colouring and in permanent magnets. The unique properties of REE (nuclear, metallurgical, chemical, catalytic, electrical, magnetic and optical) make them indispensable and non-replaceable in these applications. Novel materials using REEs are known to be more efficient, have superior performance and meet the demand for faster, smaller and lighter products with longer battery life. An integral component of modern electronic devices is REE magnet, which is tiny and at the same time ten times stronger than regular magnets and has the ability to

withstand demagnetization at elevated temperatures. If not for the miniaturization of electronic gadgets using tiny but powerful REE magnets, devices like laptops and smartphones would be prohibitively bulky and heavier. Compact fluorescent lamps (CFL) made of REE components are more energy efficient, whereas light emitting diode (LED) lighting using REEs is 80% more efficient than incandescent lighting and 40% more efficient than even CFL; besides CFL and LED lamps have much longer useful life. REEs are indispensable for green technologies such as wind turbines and hybrid motor vehicles wherein powerful REE magnets, which considerably reduce friction, form vital components. REEs continue to find newer applications in the industry: magnetic refrigeration using REE magnets is going to revolutionize refrigeration technology. An emerging application of REE in the medical field is in the treatment of kidney stones (urolithiasis): the property of REE salts to bind dietary oxalate has promises in the treatment of urolithiasis by administration of La salts that would prevent oxalate absorption into the gastro-intestinal tract. REEs also find use in guided missiles that require high-strength materials capable of functioning under very high stress and samarium alloys are aptly suited for the application<sup>2</sup>. Applications of REE metals and alloys in modern technology are expanding and their uses in defence technologies are being kept under strategic governmental wraps<sup>3</sup>. Recent synthesis of hetero-metallic hydride clusters using REEs has potential in providing a solution to the gas storage problem while using  $H_2$  as an environment-friendly future fuel<sup>4,5</sup>, since REE metal hydrides take a thousand times less space to store  $H_2$ .

Rare earths are large-ion-lithophile elements incompatible in the structure of upper mantle minerals and are thus fractionated into the earth's crust<sup>1</sup>. Though they are more abundant compared to metals like Cr, Ni, Cu, Zn, Mo, Sn, W or Pb in the earth's crust, they do not manifest any tendency to concentrate and form economic mineral deposits unlike the base metals or iron ores. More so is the case with the more valuable and desirable heavy REEs (HREEs) which have diverse applications in industry. This is because of their property called lanthanide contraction, wherein the ionic radii of REEs decrease with atomic number. In other words, the light REEs (LREEs) have larger ionic radii than the HREEs. As a result, the LREEs easily get into the melt phase and eventually are concentrated in crustal rocks, while the HREEs are left in mantle minerals during partial melting of the upper mantle. Because of the dispersed nature of REE minerals in rocks, geological exploration to locate REE deposits is a daunting task.

Beneficiation of REE minerals mined from primary rocks is a cumbersome process<sup>6</sup>, first because REE minerals do not occur concentrated in any rock requiring mining and crushing of large volumes of the rock; secondly because many other minerals also occur associated with REE minerals and thirdly associated radioactive U and Th pose problems of beneficiation and safe handling. Isolation of the individual REEs after beneficiation of the ore is again a cumbersome process owing to their similar chemical properties. Quite often the beneficiated ores have to pass through hundreds of separation cycles. The whole process of mining and processing of REEs is thus environmentally hazardous as it produces enormous mine waste,

toxic and reactive effluents and radioactive tailings. It is due to this reason that the western countries consider extraction of REEs a 'dirty business'<sup>7</sup> and are comfortable importing cheap REEs from China. It took them nearly two decades to wake up to the reality that the future of their electronic industry is in the hands of China, which is now in a position to dictate not only the prices of these metals but how much of their precious REE resource should be parted to others. Failure of finding suitable substitutes to these metals is another advantage that China enjoys.

There are more than 200 minerals containing essential or significant REE<sup>1</sup>. But bastnaesite (Ce,La) (CO<sub>3</sub>) (OH,F); xenotime (YPO<sub>4</sub>) and monazite (Ce,La,Nd,Th)PO<sub>4</sub> are the three most economically significant REE minerals. Eudialyte Na(Ca,La)<sub>2</sub>(Fe,Mn,Y)ZrSi<sub>8</sub>O<sub>22</sub>(OH,Cl)<sub>2</sub>; loparite (La,Na,Ca)(Ti,Nb)O<sub>3</sub> and allanite (Ce,Ca,Y)<sub>2</sub>(Al,Fe<sup>3+</sup>)<sub>3</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH) are less important REE minerals. REE-carbonates and phosphates are better amenable to beneficiation than REE-silicates. Allanite is an accessory mineral widely dispersed in granitic rocks and is usually produced as a by-product of uranium mining.

REE minerals occur in diverse types of igneous, sedimentary and metamorphic rocks. Often many REE minerals occur in complex associations in these rocks. The chief geological environments where they are known are the following<sup>1</sup>:

(i) Carbonatites: carbonate-rich rocks of magmatic origin and related rocks such as syenites, nepheline syenites and nephelinites; these rocks house many REE minerals such as bastnaesite, monazite, apatite and uncommon REE minerals like loparite and perovskite. (ii) Beach placers containing detrital REE minerals, monazite and xenotime, associated with other heavy minerals like ilmenite and rutile. (iii) Peralkaline granitic and syenitic igneous rocks contain the REE minerals monazite, eudialyte, allanite, loparite, xenotime, bastnaesite, allanite, etc. (iv) Iron-REE deposits, hematitic granite breccia-style deposit; extremely fine-grained monazite and bastnaesite are the chief REE minerals in this kind of deposits. (v) Pegmatites, hydrothermal quartz and fluorite veins contain monazite and euxenite. (vi) Skarn deposits typically have apatite and allanite. (vii) Residual laterites enriched in REEs. (viii) Residual REE-bearing

clay deposits, termed as 'ion-adsorption clays', where the REEs occur as ions adsorbed onto clay minerals.

In addition, sedimentary phosphate rocks called phosphorites contain REEs, chiefly the LREEs, La, Ce and Nd in the mineral francolite (carbonate-rich fluorapatite), wherein bivalent lanthanides substitute for Ca<sup>2+</sup>.

Almost 97% of the world production of REEs today comes from China. According to USGS<sup>8</sup>, China produced 1,30,000 tonnes of REEs in 2010, while the share of the rest of the world was a mere 3600 tonnes of which India accounted for 2700 tonnes. The known world reserves of REEs are 110 million tonnes, nearly half of which is in China<sup>8</sup>. Following a maritime dispute with Japan, which buys roughly 50% of Chinese REE exports, China has considerably reduced export of REE since 2010 to the bewilderment of Japan and the industrialized western countries. If China stops export completely by 2012, as is feared, Japan and the western world will quickly run out of REEs, crippling their electronic industry. Many REE mines in the West had to be closed when cheap REEs from China flooded the market by the 1990s (ref. 9), so much so that China now holds the monopoly in the production and export of these critical metals.

As a consequence of these developments, the entire world is vigorously exploring for REEs and many mines long closed are being reopened in an attempt to counter China's dominance<sup>10</sup>. The exploration effort is paying back in terms of several new discoveries, the most promising one being in Afghanistan, where USGS geologists have identified a million tonnes of REE ore within the Khanneshin carbonatite complex of the Helmand Province<sup>11</sup>. But any new mine would require 5–10 years to reach the production stage, which means China's preeminence in REE production and supply would continue for another decade. Over the last few decades, China has mastered the techniques of not only mining, processing and isolation of REEs, but their application in electronic industries too. China is also the major producer of REE magnets, the demand for which is likely to leapfrog with the world poised for greener technologies. The fact that more than 2000 chemists and technicians in China are reported to be engaged in R&D activities in their national laboratories related to the applications of REEs

speaks volumes about China's hold on these metals. Emphasizing China's monopoly in this field, the former Chinese leader Deng Xiaoping is reported to have declared in 1992 that, 'The Middle East has its oil, China has rare earths'. No wonder, if China continues to impose the export embargo, electronic industries in the rest of the world will have to move out of their present locations to China, a situation that China would readily welcome for technological and political advantage. But what worries multinational REE mining companies is the likely fall in prices of REEs in international markets, if China floods the market once again, leading to closure of mines, throwing the mining companies out of business.

It is in this context that India should hasten its plans for exploring for REE minerals. Presently known resources of REEs in India are confined to the monazite placer sands of the east and west coasts. Monazite contains mainly the LREEs, whereas deposits containing HREEs have not yet been identified in the country.

More than 40 carbonatite-alkaline plutons are known in the eastern and southern peninsular India<sup>12</sup>, which should form the primary targets for REE exploration. The Amba Dongar and Phenai Mata carbonatite complexes in Gujarat, carbonatites of Sevathur and Jokipatti, and Sivamalai in Tamil Nadu, the alkaline provinces of the Shillong Plateau and the alkaline rocks of Cuddapah basin and Khammam District in Andhra Pradesh should be re-examined for REE mineralization. The Sung valley alkaline complex in Meghalaya, an apatite-bearing rock complex, hosts a geologically suitable environment for REE mineralization. It is understood that a programme for REE exploration by the Geological Survey of India (GSI) in the Sung valley is already underway. Carbonatite-alkaline complexes of Mikir Hills, Assam and many alkaline plutons reported from Kerala are also potential targets. Besides, there are unreported 'carbonatite-like' rocks in the country. For instance, there is an occurrence near Nilambur in Kerala, which should also be covered under such surveys.

Beach placers of the country have already been studied by the Atomic Minerals Directorate and National Institute of Oceanography (NIO), and extension of the on-land placers in the offshore

domain by GSI, leaving little scope for locating new placer deposits.

The last two types of geological environments mentioned above have not been targeted for exploration in India and there is plenty of scope for searching REEs in these two environments. The ion-adsorbed clay-type of REE deposits occur extensively in tropical southern China, forming a major source of REE mined over there. These deposits are formed by leaching of REEs from primary rocks during tropical weathering that get adsorbed onto clays lower in the weathering profile. Such type of REE mineralization is rare and is known only from China and recently from Laos. This is the second most important source of REEs produced in China, besides the carbonatite-hosted Bayan Obo mines in the autonomous province of Inner Mongolia. The ion-adsorbed clay deposits have certain advantages over carbonatite-hosted deposits in that the metals are in soft materials, mining would be easier and shallow, and extraction technology is much simpler: the REEs here are in the ionic state and can be easily separated from the clays by acid leaching; further they are free of U and Th, making metallurgy safe.

Lateritic deposits that occur over low-grade primary sources such as carbonatites and syenites are potential places to look for REE minerals in India. Ion-adsorbed clays developed over REE-bearing primary rocks are other potential places to focus exploration. Primary kao-

linite is abundant at the base of laterite profiles in the west and east coasts, developed over diverse rock types and over Deccan basalts in central India. These clays should also form targets for reconnaissance REE surveys.

Some Japanese geologists have recently discovered huge deposits of REE-bearing pelagic clay sediments in the Pacific seafloor, 4000–5000 m deep (ref. 13). They are similar to the ion-adsorbed clays, but mining them poses environmental and political challenges. Nevertheless, pelagic red clays common in the deep sea should be routinely analysed for REEs by our marine exploration agencies like GSI and NIO, besides the offshore phosphatic sediments. The phosphorite deposits known from different states such as Rajasthan, Uttar Pradesh and Tamil Nadu also need to be reconnoitered for REEs.

At present, India does not have any large REE-based hardware industry. Like China, we should contemplate utilizing our REE resources for developing the domestic electronic hardware industry. However, this is an uphill task as the Chinese experience shows. What is required at the moment, however, is to intensify efforts to locate new resources of these strategic metals.

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