

RARE EARTH ELEMENTS BRIEFING NOTE



The
Geological
Society

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Introduction

The rare earth elements have long been recognised as useful because of their unusual chemical and physical properties. Their natural occurrence is strongly dependent on geological circumstances, and only in a few locations are they found in sufficient quantity and concentration, and in a suitable form and setting, to make their extraction and exploitation economically viable. The rare earth elements have also been of long-standing interest to geologists as tools for furthering scientific research into the origins of rocks and ores and into the chemical behaviour of ocean waters.

In recent years, the variety of high-tech applications of rare earth elements has burgeoned, especially in low-carbon technologies, and demand for them has grown rapidly – a trend which is expected to continue. At the same time, there is international concern about the security of their future supply, their costs, and the impacts this might have.

In light of this increased interest, the Geological Society has decided to produce this briefing note, to help to inform debate among scientists, policy-makers, potential investors and other industry players. It is presented as a series of questions and answers that deal with the properties, occurrence, extraction, supply and uses of the rare earth elements. Our focus is on their geological aspects, and the relationship between these and other scientific, economic and political considerations – we have not attempted to address in detail these non-geological issues. It is intended to be read by non-geologists with an interest in the rare earth elements, and by geologists who do not specialise in this area. Some suggestions for further reading are provided at the end of the document, for those who wish to explore further.



Statue of Professor Ding Daoheng, who discovered the Bayan Obo deposit in 1927
Photo credit: Paul Henderson

What are the rare earth elements?

The rare earth elements (REE) are a group of seventeen metallic elements - the fifteen lanthanides, with atomic numbers 57 (lanthanum, La) to 71 (lutetium, Lu), together with yttrium (Y, atomic number 39) and scandium (Sc, atomic number 21). All have similar chemical properties. The lower atomic weight elements lanthanum to samarium (Sm), with atomic numbers 57 to 62, are referred to as the light rare earth elements (LREE); while europium (Eu) to lutetium, with atomic numbers 63 to 71, are the heavy rare earth elements (HREE). (The dividing line drawn between LREE and HREE can vary somewhat, and the term 'mid REE' is also now sometimes used.) Yttrium, although it has a lower atomic weight, is grouped with the HREE because of its chemical similarity. Scandium's properties are different enough from those of the other REE that most of the scientific and general literature excludes it and focuses on the lanthanides and yttrium – we have followed that convention here.

How rare are they?

The term 'rare earths' was first used in the late eighteenth and early nineteenth centuries, to refer to minerals containing REE and some other metals, known deposits of which were rare – only subsequently did the name 'rare earth elements' come to be associated solely with the specific set of elements it denotes today. In fact, in terms of their overall abundance in the Earth's crust, the REE are not particularly rare. On average, as a proportion of the Earth's continental crust, Cerium (Ce) is the most abundant, at 43 parts per million (ppm), followed by lanthanum (20 ppm) and neodymium (Nd, 20 ppm). The rarest REE is thulium (Tm, 0.28 ppm), except for promethium (Pm) which is virtually absent, since it is radioactive with a short half-life. Yttrium occurs at 19 ppm. So their overall abundances are not dissimilar from many other important elements such as lithium (17 ppm), germanium (1.3 ppm), copper (27 ppm), tin (1.7 ppm) and uranium (1.3 ppm).

How do the rare earth elements behave?

The REE's distinctive properties are due to their atomic structure, especially the configuration of their electrons, which is unlike that of other elements. While many important properties are shared by all the REE, others are specific to particular elements. Because of their chemical similarities, they occur together in minerals and rocks and are difficult to separate from each other (sometimes referred to as 'chemical coherence'). However, the numerous practical uses of REE often depend on physical properties (electrical, magnetic, spectroscopic, and thermal) which are specific to particular elements, so the challenge of separating them must be overcome.

Their chemical properties depend not only on their atomic structure, but also on their size. Unusually, atomic size of the lanthanides decreases with increasing atomic number, and this results in LREE and HREE occurring in different minerals. For example, lutetium can substitute more readily for other elements in minerals where the available sites are relatively small, where the larger lanthanum ion will not fit. REE compounds are generally ionic and often very stable, as in the case of the oxides. Geologically occurring compounds tend to be oxides, halides, carbonates, phosphates and silicates, but not sulphides. Most of the lanthanides exhibit a trivalent state (i.e. Ln^{3+} , where Ln is the generic symbol for lanthanides) but cerium can also be quadrivalent (Ce^{4+}) and europium is often divalent (Eu^{2+}).

Five of the rare earths (excluding promethium) each contain a proportion of a radioactive isotope (^{138}La , ^{144}Nd , ^{147}Sm , ^{152}Gd , ^{176}Lu).

The rare earth elements are attracting a lot of current interest – why?

The REE have many important uses, and global production has increased rapidly in recent years from about 80,000 tonnes of rare earth oxides in 2000 to 123,000 tonnes in 2009, an increase of more than 50%¹. Demand is expected to continue to grow, especially because of their use in low carbon technologies. In 2009, China produced around 97% of global REE, and recent reductions in Chinese export quotas have led to greatly increased prices internationally, and concern over future security of supply. There is particular concern that the development and uptake of new green technologies may be constrained by the availability of these raw materials. Prices of REE have been volatile, and have increased rapidly – for example, the global price of cerium oxide in July 2011 was 38 times greater than its average price in 2009².

This has led some governments to evaluate the likelihood of a shortfall in supplies, and the risks this would pose to their industries. The European Union carried out a major evaluation, presented in June 2010, to identify 'critical' minerals and metals – that is, those which combined the highest supply risk and economic importance, coupled with low potential to be substituted by other resources, and low recycling rates. This identified the REE as among the 14 mineral commodities most critical to the EU economy (the REE were considered as a single entity for the purposes of the evaluation). A similar US study reached similar conclusions. Some governments are developing policies aimed at securing adequate and stable future supplies for their industries. Although the focus differs from country to country, particular emphasis is being given to achieving more globally diverse supplies; to improving recycling, re-use and resource efficiency (doing more with less); and to identifying substitutes.

Investors and mining companies are also taking a renewed interest in REE, as increased prices (and in some cases government incentives) make exploitation of resources potentially more profitable. However, the relatively small global market for REE limits the commercial attractiveness of starting up new mining operations. Understanding the geology of REE, and the extent of known or possible resources, are among many factors that influence companies' decision making.

What are the uses of rare earth elements?

With new and developing technologies, the uses of REE have extended from well-established applications such as glass polishing, to include high-performance magnets, high-tech catalysts, electronics, glass, ceramics, and alloys^{3,4}. An increasingly important area of REE use is in low-carbon technologies. Large wind turbines can each use up to 2 tonnes of high-strength magnets which contain about 30% REE⁴. Up to 20 kg of REE are used in the batteries, electric traction motors and regenerative braking systems of each hybrid vehicle. The main applications of REE are shown in the table below.

Demand for REE in all these applications is expected to continue to increase over the next few years, particularly in the manufacture of magnets.

Many of these uses depend on the distinctive properties of REE (individually or as a group) referred to above. Their use in LCD and plasma screens, for example, depends on their spectroscopic properties – europium (as Eu^{3+} , in the solid state) exhibits red luminescence, while terbium's (as Tb^{3+}) is green. The thermal properties of REE lend stability to alloys under high stress and temperature, for instance in jet engines.

Application ^{3,4,5,6} :	Magnets	Catalysts	Alloys	Glass and Electronics	Miscellaneous
Global consumption (thousands of tonnes) (2008) ⁷ :	26.3	25.0	22.3	36.0	14.5
Principal REE ^{3,4,5,6} (main elements shown in bold):	Dysprosium Gadolinium Neodymium Praseodymium Samarium Terbium	Cerium Lanthanum	Cerium Dysprosium Lanthanum Neodymium Praseodymium	Cerium Europium Gadolinium Lanthanum Neodymium Praseodymium Terbium Yttrium	All
Examples of use ^{3,4,5,6} :	Electric motors in hybrid vehicles; Wind power generators; Hard disc drives; CD and DVD players; Imaging; Portable electronics; Microphones and speakers; Magnetic refrigeration.	Petroleum refining; Catalytic converters; Diesel additives.	NiMH batteries; Fuel cells; Other alloys (with iron, magnesium, aluminium and in special steels).	Display phosphors (compact fluorescent lamps, LCD and plasma screens, cathode ray tubes, medical imaging); Lasers; Fibre optics; Glass polishing and tinting.	Ceramics; Water treatment; Nuclear fuel rods; Pigments; Fertiliser; Medical tracers.

Are the rare earth elements useful in scientific research?

The properties of the REE have led to them being successfully applied to numerous geological research problems. The distribution of REE in a series of igneous rocks, for example, can indicate details of their origins and history, as well as their relationship to one another. The same techniques can be applied to cosmic materials. It has been shown that some meteorites (achondrites) were formed by processes very similar to those by which many igneous rocks on the Earth are made (fractional crystallisation).

The existence of multiple valencies of some REE, and their different chemical behaviour, can also help to reveal geological processes, if the relative proportions of, say, Eu^{2+} and Eu^{3+} are different from the background level (a so-called 'abundance anomaly'). An instance of this is on the moon – strong but opposite europium anomalies in the rocks of the lunar highlands and the mare basalts have provided useful information on their origins.

The REE's radioactive isotopes have long half-lives. This makes some of them (with their daughter products) very suitable for geochemical and petrological studies, especially ^{138}La - ^{138}Ce , ^{147}Sm - ^{143}Nd , and ^{176}Lu - ^{176}Hf . They are used extensively in the dating of rocks, particularly ancient ones and high-grade metamorphics. They are also used in investigating problems such as ocean mixing, the mixing of magmas, or contamination of the Earth's mantle by rocks from the crust.

Where are rare earth elements found?

In looking for concentrations of any element that might be of economic interest, there are several factors to consider: the minerals in which they occur, and how easily the element can be extracted; the types of rock in which these minerals are found; the most promising geological settings in which to explore for these rocks; and the particular locations of mineral deposits which are capable of being mined and processed economically.

In which minerals do rare earth elements occur?

Over 200 rare earth minerals have been described. However, in many cases there are no concentrations of these minerals that are economic to mine and in others there is no known method to extract the REE from the mineral economically.

Minerals tend to be rich in either LREE or HREE, but generally include most of the REE in some quantity, if only at minor or trace levels. The proportions of the different REE within minerals vary between deposits.



Monazite-(Ce) specimen from Siglo XX mine, Bolivia – the orange mineral is monazite, and the clear one quartz
Photo credit: Natural History Museum (specimen no: BM 1972,348)

The name of a REE mineral often indicates, by use of the chemical symbol, the most abundant element. For example, in bastnäsite-(Ce), cerium is present in the largest quantity (it also contains significant amounts of lanthanum, neodymium and praseodymium). Bastnäsite-(Ce) is the most common but bastnäsite-(La) and bastnäsite-(Nd) also occur. (Chemical formulae are often written in an 'idealised form', with the mixture of REE represented by the dominant element. So, bastnäsite-(Ce) is given as CeCO_3F .)

The most important rare earth minerals in ore deposits are bastnäsite and monazite-(Ce) (CePO_4). Each contains about 70% rare earth oxides by weight. Other significant ones are the carbonates parisite-(Ce) and synchysite-(Ce) (often found intergrown with bastnäsite), and the phosphate xenotime-(Y). The complex silicates allanite-(Ce), eudialyte and steenstrupine also contain significant amounts of REE, as do the carbonate ancylite-(Ce) and the phosphate churchite-(Y).

Minerals that contain much smaller amounts of rare earth elements can act as important sources. For example, the oxide loparite-(Ce), mined in Russia for its niobium, also contains about 1% rare earth oxide by weight – enough to make REE worthwhile extracting. Fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) can sometimes also be a source of rare earths. If mined as a source of phosphorus for fertiliser, it is possible to extract REE as a by-product.

In which types of rock do these minerals occur?

REE are found principally in carbonatites. These are igneous rocks comprising more than 50% carbonate minerals, principally calcite (calcium carbonate), but in some cases magnesium-bearing carbonates (dolomite, magnesite) or iron-bearing carbonates (siderite), that crystallised from a high-temperature liquid from deep in the Earth. Carbonatites almost always contain REE, which constitute about 3,500 ppm of these rocks, so they are the most obvious place to look for REE.

REE are found in high concentrations in some, but not all, alkaline igneous rocks (which make up only about 0.5% of all igneous rocks). They are characterised by their high contents of alkali metals.

There are also some secondary deposits of REE. These are essentially produced by weathering of primary sources and their subsequent concentration by physical or chemical means. 'Placer' deposits are produced by physical concentration of rare earth and other heavy minerals from weathering; 'laterite' deposits result from enrichment of REE by *in situ* chemical alteration. There is one known example of a further type of secondary deposit, known as ion-adsorption clays, in China. The REE in these deposits were released by weathering of REE-rich granites and subsequently adsorbed by clay minerals.

There are also some rare earth mineral concentrations of economic interest in granite pegmatites and some hydrothermal (hot water) vein systems. Researchers have recently found elevated concentrations of REE in deep sea mud in the Pacific Ocean, which may also constitute a potential resource.

In what kinds of geological environment are these rocks found?

The carbonatites and alkaline igneous rocks are characteristically found in the interiors of tectonic plates, that is, away from the active plate margins where volcanic activity is at its greatest. They

are commonly associated with the major rift systems, such as the East African and Baikal rifts and the Rhine Graben. The carbonatites are mostly confined to continental areas, while the alkaline rocks also occur over much of the world's oceanic intraplate areas on volcanic islands. Although more than two thirds of carbonatites that have been dated are Phanerozoic in age (less than 500 million years), they are overwhelmingly concentrated in areas comprising older Precambrian rocks.

Can all rare earth element deposits be exploited economically?

Only a small proportion of REE deposits are of sufficient size, type and concentration that they can be exploited economically using existing technology. These are referred to as 'reserves'. Which deposits are considered to be reserves will depend not only on fixed factors (geographical distribution and concentration; mineral type), but also on variable ones (commodity prices; regulatory regimes including environmental protection; improved technology for extraction and processing). Reserves can also grow with the discovery of new exploitable resources, which is dependent on both research and exploration work. Since ores containing REE tend to be rich in either LREE or HREE, their relative value will vary according to market factors.

Where are the main deposits?

The main reserves are in China (including Bayan Obo), the CIS (in Russia, Kyrgyzstan and Kazakhstan), the USA (including Mountain Pass) and Australia (including Mount Weld). There are also resources in India, Vietnam, Malaysia, Thailand, Indonesia, South Africa, Namibia, Mauritania, Burundi, Malawi, Greenland, Canada and Brazil⁸.

Bayan Obo in Inner Mongolia, China, contains the greatest quantity of REE known. It is an iron-rich deposit hosted in dolomite, the origin of which is still a subject of debate. However, the Maoniuping occurrence (Sichuan Province) is at present the world's biggest REE producer, mainly because the REE minerals have proved to be easy to concentrate by gravitational methods. The Weishan deposit (Shandong Province) is also mined for REE. The REE at Maoniuping and Weishan are also found in carbonatite dykes.

Before Bayan Obo came on stream, the largest single source of REE was a carbonatite sheet at Mountain Pass in California, USA. Although mining at Mountain Pass ceased in 2002, it has recently restarted and is expected to return to full production level in 2012. Mountain Pass is expected to make a significant contribution to global supply, as are the deposit in weathered carbonatite at Mount Weld, in Western Australia; the alkali trachyte intrusion at Dubbo, New South Wales, Australia (where REE will be co-produced with zirconium and other metals); and a further smaller monazite deposit at Steenkampskraal, Western Cape, South Africa.



Mount Weld, Western Australia

Photo credit: Matthew Demmer, Camborne School of Mines, University of Exeter

Significant mineral sand deposits include those in western India (still in production) and in western Australia. Most of these deposits contain monazite-(Ce) and some also contain xenotime-(Y). REE are also produced as by-products from the minerals apatite (phosphate ore) and loparite (niobium ore) mined at Khibiny and Lovozero on the Kola Peninsula, Russia.

A 2002 report by the United States Geological Survey listed 822 occurrences of REE in a wide variety of rock types, about 20% of which are carbonatites⁹. As at June 2011, there is also active exploration in alkaline igneous rocks, mineral sands, and hydrothermal deposits.

Are there any in the UK?

The UK has few REE resources, but little systematic exploration has been carried out. The most attractive targets are the Caledonian age alkaline igneous intrusions of north-west Scotland.

How are they extracted and processed?

All rare earth mines are open cast except for a few where REE are produced as a by-product, such as at Lovozero in Russia. Most employ standard large-scale mining techniques, involving 'drill, blast and haul operations'.

Separation of the ore from waste material is done by a variety of techniques. For example, bastnäsite is mostly separated by froth flotation. Monazite can be treated in a similar way, but can also be concentrated along with other heavy minerals from mineral sand deposits using gravity separation; and then separated from the other heavy minerals by high-intensity magnetic and electrostatic methods.

Once a mineral concentrate has been produced, the REE are extracted from it by a series of steps. These may include 'cracking' (roasting, usually with acid or alkali, or treating with a hot solution), leaching or solution using a range of solvents, chemical precipitation and evaporation. The process can be complex, involving multiple stages to separate each of the REE, and varies from case to case. Maximum value is derived by producing individual REE metals but this is expensive and time consuming. Many REE are traded as the cheaper REE oxides, which are suitable for much industrial use.

In some deposits, REE are not mined, but are leached in situ by passing solvents through the rock.

There are many known minerals which contain some REE, but in most cases neither the minerals nor the REE themselves can yet be economically extracted and separated.

What are the environmental effects of rare earth production?

The frequent association of the radioactive elements thorium and uranium with REE deposits is one of the main environmental problems. The heavy REE in particular tend to concentrate in the same geological environments as thorium. A few percent of thorium by weight is common in monazite formed in granitic rocks, and in the mineral sands derived from them. These marine and alluvial placer deposits used to be the most important source of REE during the 1950s and 1960s. However, they have generally fallen from favour because of their radioactivity. Other deposits, such as those associated with carbonatite rocks, have much lower levels of thorium.

In common with most mining and processing, REE production uses a great deal of energy. Where the energy is derived from fossil fuels, this will add to carbon emissions (in the absence of widespread Carbon Capture and Storage) – especially if much of it comes from coal-fired power stations, as currently in China.

Other environmental problems can arise from the extraction and processing of REE, including pollution from the chemicals used. These are often the result of inadequate environmental regulation or enforcement.

Is their availability sufficient and secure?

This is a very difficult question to answer. As at July 2011, the main problem with REE supply is that there are not enough REE available to countries other than China. Although there are known REE deposits outside China that are potentially economic to mine, they cannot simply be ‘turned on’; it may take ten years, or longer, to go through all the technical, financial, environmental and regulatory stages needed to establish a new mine.

REE resources are widely distributed across the globe, so geological scarcity in absolute terms is not likely to be a concern. Currently, there is considerable exploration activity for REE worldwide, with numerous companies, most of them relatively small, engaging in exploration on every continent. As at July 2011, mining has resumed at Mountain Pass and started at Mount Weld, both of which are expected to reach full production levels in 2012. Together, these two deposits could add 40,000 tonnes per annum to global supplies. If the market outlook remains positive and prices remain high then global reserves will increase and new projects will likely be brought into production. In the longer term advances in science and technology will improve our ability to find and extract REE, as has been the case for other metals in the past, and the likelihood of supply disruptions will be reduced.

There are many variables that influence the future supply-demand balance for REE, collectively and individually, and make it difficult to predict shortfalls in supply. In the medium and longer term, it is expected that adequate supplies of most REE will be available. However, over the next decade, up to 2020, shortages are predicted for some, notably neodymium, dysprosium, europium, terbium and yttrium. The magnitude and duration of such shortages will depend on how successful exploration projects are, as well as on complex interconnected market and regulatory factors.

Various governments and industrial users worldwide have begun to develop strategies to safeguard the REE supplies that they need. Governments are working individually and together to develop an early warning system to better predict future supply problems for REE and other critical metals. Some industrial users of REE have established joint venture partnerships with mining companies, thereby ensuring a market for the ores at a known price and securing supply for the processor/manufacturer (see Ernst and Young, September 2010¹⁰ and April 2011¹¹ for examples).

Are there alternatives to mining rare earth elements?

Although various methods of recycling are proven, little rare earth recycling takes place¹². Reasons for this include lack of infrastructure, the need for extensive further work to develop recycling techniques, low concentrations in scrap, and products not being designed to allow

efficient recovery at the end of their life (with little incentive at present for manufacturers to improve design in this respect)¹³. Scope for recycling is also limited by the fact that the likely future demand for some REE is large compared to the amount already in circulation, and by the long lifetimes of some of the products in which they are used. At present, Japan is the only significant centre for research into recycling techniques, with Hitachi, for instance, aiming to recycle electric motor magnets by 2013^{6,13}.

There is some scope for substituting REE with other elements in many applications. However, the substitutes are generally less effective^{6,13,14}. For example, no magnets have yet been developed with strength comparable to those made using neodymium⁶. Large scale substitution would not necessarily solve problems of supply, because although the demand for REE would be reduced, the demand for substitute materials would increase. Another possible area of design innovation is resource efficiency, or 'doing more with less' – that is, reducing the amount of REE which is required to produce each unit of the technology in question.

A separate alternative to substitution and recycling of rare earths is to evaluate potential novel, previously unconsidered, resources such as waste materials from mining operations for other commodities and from industrial processes. 'Secondary' resources of these types not only have the potential to extend the resource base for REE, but also have a smaller environmental footprint than exploiting primary ores, maximising the efficiency of resource use and reducing the amount of potentially harmful waste from industrial processes. Research is underway to investigate the concentrations of REE found in several industrial waste streams, and the potential for their economic extraction.

Nonetheless, it is likely that, given the escalating demand for REE, mining of primary ores will continue to provide the lion's share of supply.

Conclusions

Rare earth elements will continue to be of considerable interest for the foreseeable future, with demand likely to grow. While market mechanisms should ensure that serious shortages are averted, at least in the long term, there may be significant short-term disruptions to the supply of some REE, especially HREE, and price instability.

Geological and mineralogical research should continue to play an important role in the search for rare earth ore deposits and their extraction, ensuring that as little damage is done to the environment as possible. With the renewed focus on REE by policy-makers and investors, in order that decision making is informed by the best available science, it is important to ensure sustained funding of research on the entire life cycle of the REE, from exploration and mining to manufacture, recycling, re-use and disposal. It is also essential to gather and maintain reliable and comprehensive information on REE geology, deposits, resources, reserves, production, trade and consumption.

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