British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Rare Earth Elements

June 2010

Definitions, mineralogy and deposits

Definitions and characteristics

The rare earth elements (REE) (sometimes referred to as the rare earth metals) are a group of 17 chemically similar metallic elements, including scandium, yttrium and the lanthanides. The lanthanides are elements spanning atomic numbers 57 to 71 (Table 1). They all occur in nature, although promethium[1], the rarest, only occurs in trace quantities in natural materials as it has no long-lived or stable isotopes (Castor and Hedrick, 2006). Scandium and yttrium are considered REE as they have similar chemical and physical properties. Separation of the individual REE was a difficult challenge for chemists in the 18th and 19th centuries, such that it was not until the 20th century that they were all identified. Because of their chemical similarity the REE, can very easily substitute for one another making refinement to pure metal difficult.

The term rare earth is a misnomer arising from the rarity of the minerals which they were originally isolated from. In contrast REEs are relatively plentiful in the earth's crust having an overall crustal abundance greater than silver and the more abundant REE have similar crustal abundances to copper (50 ppm) and lead (Harben, 2002; USGS, 2002). The crustal abundance of individual REE varies widely, from cerium the most abundant at 33 ppm to lutetium with a concentration of 0.3 ppm (Taylor and McLennan, 1985).

The lanthanides are commonly divided into: the light rare earth elements (LREE) – lanthanum through to europium and the heavy rare earth elements (HREE) – gadolinium through to lutetium (Table 1). The relative abundance of the REE varies considerably and relates to two main factors. REE with even atomic numbers have greater abundance than their odd numbered neighbours. Secondly the lighter REE are more incompatible and consequently more strongly concentrated in the continental crust than

Element	**Symbol**	**Atomic number**	**Atomic weight**	**Density** (gcm^{-3})	**Melting Point (°C)**	**Vicker's hardness, 10 kg load,** kg/mm^2
Scandium	Sc	21	44.95	2.989	1541	85
Yttrium	Y	39	88.90	4.469	1522	38
Lanthanum	La	57	138.90	6.146	918	37
Cerium	Ce	58	140.11	8.160	798	24
Praseodymium	Pr	59	140.90	6.773	931	37
Neodymium	Nd	60	144.24	7.008	1021	35
Promethium[1]	Pm	61	145.00	7.264	1042	-
Samarium	Sm	62	150.36	7.520	1074	45
Europium	Eu	63	151.96	5.244	822	17
Gadolinium	Gd	64	157.25	7.901	1313	57
Terbium	Tb	65	158.92	8.230	1356	46
Dysprosium	Dy	66	162.50	8.551	1412	42
Holmium	Ho	67	164.93	8.795	1474	42
Erbium	Er	68	167.26	9.066	1529	44
Thulium	Tm	69	168.93	9.321	1545	48
Ytterbium	Yb	70	173.04	6.966	819	21
Lutetium	Lu	71	174.97	9.841	1663	77

Table 1 Selected properties of the REE. Compiled from Gupta and Krishnamurthy (2005).

Elongate prismatic fergusonite in an open cavity associated with albite and quartz, Arran, Scotland. Photograph: Fergus MacTaggart, BGS © NERC.

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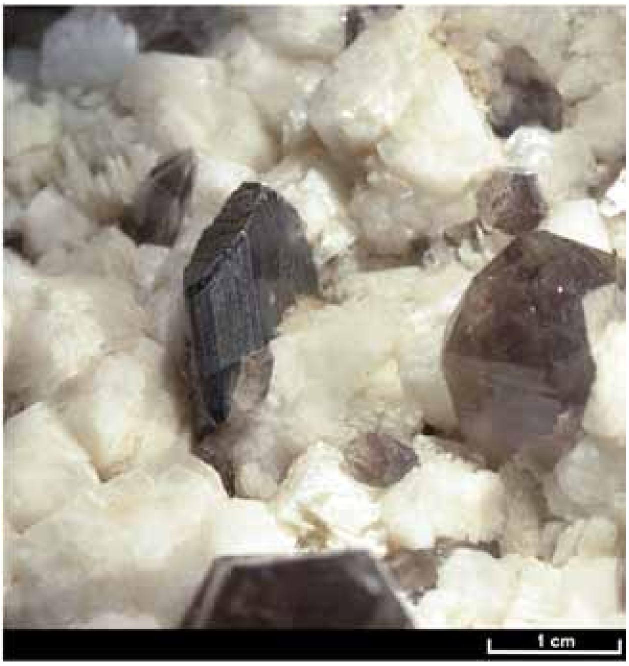
[1] Promethium: is a radioactive element.

Mineral	Formula	Approximate REO %
Aeschynite-(Ce)	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$.	32
Allanite-(Ce)	$(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$.	38
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	19
Bastnäsite-(Ce)	$(Ce,La)(CO_3)F$	75
Brannerite	$(U,Ca,Y,Ce)(Ti,Fe)_2O_6$	9
Britholite-(Ce)	$(Ce,Ca)_5(SiO_4,PO_4)_3(OH,F)$	32
Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)$ $ZrSi_8O_{22}(OH,Cl)_2$(?).	9
Euxenite-(Y)	$(Y.Ca.Ce,U,Th)(Nb,Ta,Ti)_2O_6$	24
Fergusonite-(Ce)	$(Ce,La,Nd)NbO_4$	53
Gadolinite-(Ce)	$(Ce,La,Nd,Y)_2Fe^{2+}Be_2Si_2O_{10}$.	60
Kainosite-(Y)	$Ca_2(Y,Ce)_2Si_4O_{12}CO_3.H_2O$.	38
Loparite	$(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$	30
Monazite-(Ce)	$(Ce,La,Nd,Th)PO_4$	65
Parisite-(Ce)	$Ca(Ce,La)_2(CO_3)_3F_2$.	61
Xenotime	YPO_4.	61
Yttrocerite	$(Ca,Ce,Y,La)F_3.nH_2O$.	53
Huanghoite-(Ce)	$BaCe(CO_3)_2F$.	39
Cebaite-(Ce)	$Ba_3Ce_2(CO_3)_5F_2$.	32
Florencite-(Ce)	$CeAl_3(PO_4)_2(OH)_6$.	32
Synchysite-(Ce)	$Ca(Ce,LA)(CO_3)_2F$.	51
Samarskite-(Y)	$(Y,Ce,U,Fe^{3+})_3(Nb,Ta,Ti)_5O_{16}$.	24
Knopite	$(CaTi,Ce_2)O_3$	na

Table 2 A selection of REE-bearing minerals. Mineral formulae sourced from Clark (1993) and estimates of REO content based on Webmineral composition, with the exception of apatite (Caster and Hedrick 2006).Where the mineral name is followed by brackets the formula is for the specific chemical variant of the mineral identified. Note one or more other chemical variants, in which the dominant element varies from the one shown, may exist. na: not available.

the REE with larger atomic numbers. The chemically similar nature (ionic radii and oxidation states) of the REE means they can substitute for one another in crystal structures. This results in the occurrence of multiple REE within a single mineral and a broad distribution in the earth's crust (Castor and Hedrick, 2006).

As refined metals the REE are lustrous, iron grey to silvery in appearance. They are characteristically soft, malleable, ductile and typically reactive. The electron structure of REE gives them some unusual magnetic and optical properties. The melting points of REE generally increase across the series, from 798°C for cerium to 1663°C for lutetium. Melting point has direct implications for the reduction process used in metal production. The REE, with the exception of Sc, Y, La, Yb and Lu, are strongly paramagnetic[2] and have strong magnetic anisotropy[3] (Gupta and Krishnamurthy, 2005).



Allanite crystal associated with albite and quartz in an open cavity, Arran, Scotland. Photograph: Fergus MacTaggart, BGS © NERC.

Mineralogy

REE do not occur naturally as metallic elements. REE occur in a wide range of mineral types including halides, carbonates, oxides and phosphates (Table 2). The REE are largely hosted by rock-forming minerals where they substitute for major ions. Higher concentrations of REE are required to form their own minerals (Möller, 1986). Around 200 minerals are known to contain REE, although a relatively small number are or may become commercially significant (Table 2). The vast majority of resources are associated with just three minerals, bastnäsite, monazite and xenotime. In some REE minerals the LREE are particularly enriched relative to the HREE, whilst in others the opposite is the case. Bastnäsite and monazite are the primary source of the LREE, mainly Ce, La and Nd. Monazite has a different balance as it contains less La and more Nd and HREE. It is also significant to note that monazite contains the radioactive element thorium. Xenotime is dominated by the heavier REE including Y, Dy, Er, Yb and Ho (Harben, 2002).

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[2] Paramagnetic: a type of magnetism which only occurs in the presence of an external magnetic field.

[3] Magnetic anisotropy: the dependence of materials magnetic properties on direction.

Major deposit classes

REE mineral deposits occur in a broad range of igneous[4], sedimentary[5] and metamorphic[6] rocks. The concentration and distribution of REE in mineral deposits is influenced by rock-forming and hydrothermal[7] processes including enrichment in magmatic[8] or hydrothermal fluids, separation into mineral phases and precipitation, and subsequent redistribution and concentration through weathering and other surface processes. Environments in which REE are enriched can be broadly divided into two categories: primary deposits associated with igneous and hydrothermal processes and secondary deposits concentrated by sedimentary processes and weathering. Within these two groups REE deposits can be further subdivided depending on their genetic associations[9], mineralogy and form of occurrence. Classification of some deposits is complicated by unclear genetic associations and/or the involvement of multiple geological processes. For example deposits associated with carbonatites can be divided into those directly associated with magmatic processes and crystallisation, others of vein/replacement types and residual/surface weathering deposits, or a combination of these.

The global distribution of selected REE occurrences, deposits and mines is shown in Figure 3. The most comprehensive listing of REE deposits and occurrences is provided by Orris and Grauch (2002) (Table 3). The most commercially important REE deposits are associated with magmatic processes and are found in, or related to, alkaline igneous rocks and carbonatites.

Primary deposits

The REE are preferentially enriched in partial melts or fluids from the upper mantle and in melts of crustal origin because of their large ionic radius[10] (Möller, 1986). Within the magmatic and hydrothermal environment REE minerals may be associated with quartz- and fluorite-bearing veins and breccia[11] zones, skarns[12] and pegmatites[13]. The economic potential of a REE deposit is strongly influenced by its mineralogy and the geological processes from which it has formed. Deposits which have a spatial and genetic association with alkaline igneous rocks can be divided into two categories, one associated with carbonatites[14] and related igneous rocks and the other with peralkaline[15] igneous rocks (Samson and Wood, 2004).

Carbonatite-associated deposits

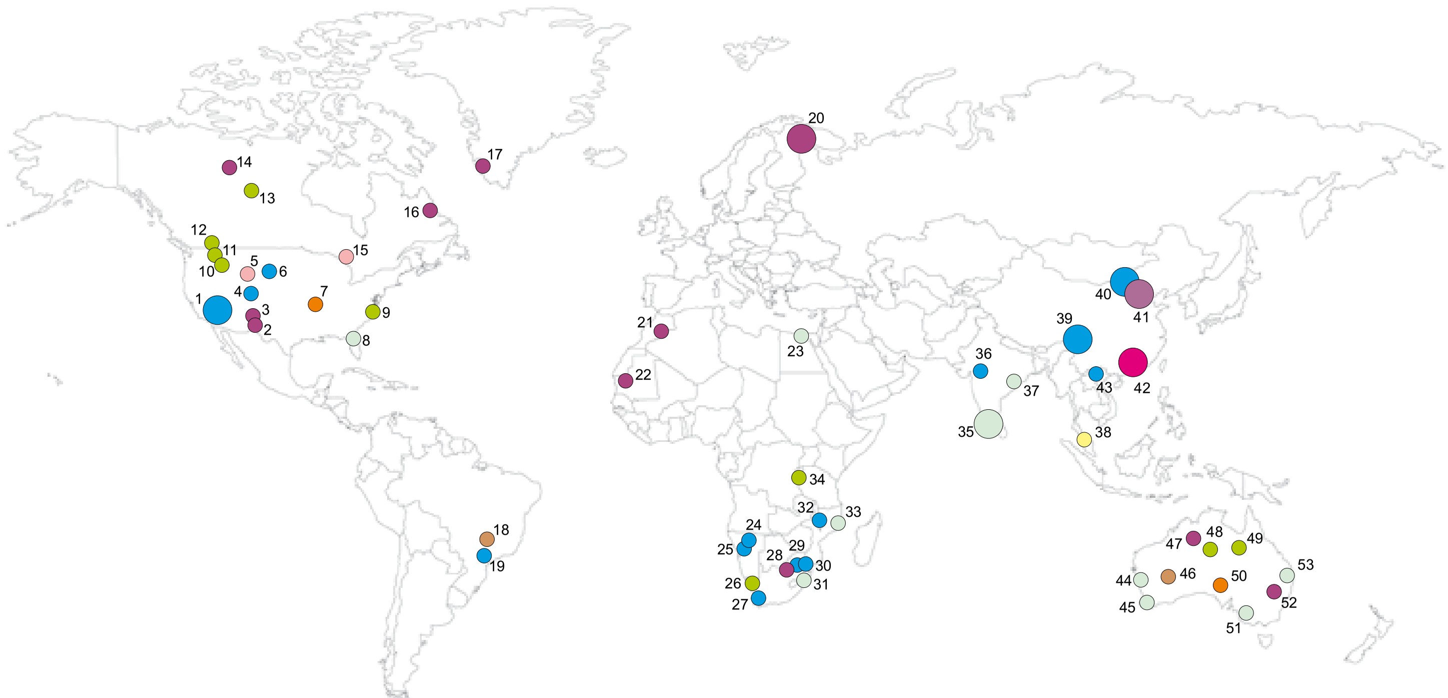
Carbonatites are igneous rocks that contain more than 50 per cent carbonate minerals. They are thought to originate from carbon dioxide-rich and silica-poor magmas from the upper mantle. Carbonatites are frequently associated with alkaline igneous provinces and generally occur in stable cratonic regions, commonly in association with areas of major faulting particularly large-scale rift structures. More than 500 carbonatite occurrences are documented worldwide, with the main concentrations in the East African Rift zones, eastern Canada, northern Scandinavia, the Kola Peninsula in Russia and southern Brazil (Woolley and Kjarsgaard, 2008). Carbonatites take a variety of forms including intrusions within alkali complexes, isolated dykes and sills, small plugs or irregular masses that may not be associated with other alkaline rocks. Pipe-like bodies, which are a common form, may be up to 3–4 km in diameter (Birkett and Simandl, 1999). Intrusive carbonatites are commonly surrounded by a zone of metasomatically[16] altered[17] rock, enriched in sodium and/or potassium. These desilicified[18] zones, known as fenite, develop as a result of reaction with Na-K-rich fluids produced from the carbonatite intrusion. Carbonatites are characteristically enriched in a range of elements in addition to carbon dioxide, calcium, magnesium and iron, including REE, barium, strontium, fluorine, phosphorous, niobum, uranium and thorium (Rankin, 2004). The REE in carbonatites are almost entirely LREE which occur in minerals such as bastnäsite, allanite, apatite and monazite (Gupta and Krishnamurthy, 2005). REE minerals commonly develop in the late stages of carbonatite emplacement. This frequently makes it difficult to determine whether the minerals were precipitated directly from the carbonatite magma or from hydrothermal fluids (Wall and Mariano, 1996).

4 Igneous: rocks which have a crystalline texture and appear to have consolidated from molten rock.
5 Sedimentary: a rock formed from sediment which may of organic or inorganic in origin,
6 Metamorphic: Metamorphic: rocks changed by temperature and pressure within the Earth's crust
7 Hydrothermal – hot fluids.
8 Magmatic: related to magma, molten rock and fluid originating deep within or below the Earth's crust.
9 Genetic associations – the geological processes associated with the formation of a mineral deposit.
10 Ionic radius: half the distance between the centres of two ions in an element.
11 Breccia: a rock that has been mechanically, hydraulically or pneumatically broken into angular fragments.
12 Skarn: a metamorphic rock that forms as a result of chemical alteration by hydrothermal and other fluids.
13 Pegmatite: a very coarse-grained igneous rock.
14 Carbonatite: a rock which contains more than 50 per cent carbonate minerals, thought to originate from carbon dioxide-rich and silica-poor magmas from the upper mantle.
15 Peralkaline: igneous rocks which have a higher molecular proportion of combined sodium and potassium than aluminium.
16 Metasomatism: chemical alteration of a rock by fluids.
17 Altered: hydrothermal or weathering induced changes to the chemical and mineralogical composition of a rock.
18 Desilicified: a rock in which silica has been released from the constituent minerals.

Deposit type	Brief description	*Number documented	Typical grades and tonnage	Major examples
Primary deposits				
Carbonatite-associated	Deposits associated with carbonate-rich igneous rocks associated with alkaline igneous provinces and zones of major faulting	107	A few 10s thousands of tonnes to several hundred million tonnes, 0.1–10% REO e.g. Bayan Obo: 750 million tonnes at 4.1% REO	Mountain Pass, USA; Bayan Obo, China; Okorusu, Namibia; Amba Dongar, India; Barra do Itapirapuã, Brazil; Iron Hill, USA
Associated with alkaline igneous rocks	Deposits associated with igneous rocks characterised by abundant alkali minerals and enrichment in HFSE	122	Typically <100 million tonnes (Lovozero >1000 million tonnes), grade variable, typically <5% REO e.g. Thor Lake: 64.2 million tonnes at 1.96% REO	Ilimaussaq, Greenland; Khibina and Lovozero, Russia; Thor Lake and Strange Lake, Canada; Weishan, China; Brockman, Australia; Pajarito Mountain, USA
Iron-REE deposits (iron oxide-copper-gold deposits)	Copper-gold deposits rich in iron oxide and diverse in character and form	4	e.g. Olympic Dam: 2000 million tonnes at 0.3295% REO (Orris and Grauch, 2002)	Olympic Dam, Australia; Pea Ridge, USA
Hydrothermal deposits (unrelated to alkaline igneous rocks)	Typically quartz, fluorite, polymetallic veins and pegmatites of diverse origin	63(a)	Typically <1 million tonnes, rarely up to 50 million tonnes, grade variable, typically 0.5–4.0%, rarely up to 12% REO e.g. Lemhi Pass: 39 million tonnes at 0.51% REO (Orris and Grauch 2002)	Karonge, Burundi; Naboomspruit and Steenkampskraal, South Africa; Lemhi Pass and Snowbird and Bear Lodge, USA; Hoidas Lake, Canada
Secondary deposits				
Marine placers	Accumulations of resistant, heavy minerals, concentrated by coastal processes and found along or close to existing coastlines	264(b)	Highly variable tonnage, commonly in the order of 10s to 1–3 hundred million tonnes, generally <0.1% monazite e.g. Jangardup 30 million tonnes at 0.046% Monazite (Orris and Grauch 2002)	Eneabba, Jangardup, Capel, WIM 150, Australia; Green Cove Springs, USA; Richards Bay, South Africa; Chavara, India;
Alluvial placers	Concentrations of resistant, heavy minerals in river channels	78(b)	10s to <200 million tonnes, typically <0.1% monazite e.g. Horse Creek: 19 million tonnes at 0.041% monazite (Orris and Grauch 2002)	Perak, Malaysia; Chavara, India; Carolina monazite belt and Horse Creek, USA; Guangdong, China
Paleoplacers	Ancient placer deposits typically forming consolidated, cemented rocks	13(b)	10s million tonnes up to 100 million tonnes, typically (<0.1% REO	Elliot Lake, Canada; Bald Mountain, USA
Lateritic deposits	Residual surface deposits formed from intense chemical weathering of REE-enriched igneous rocks	42(c)	A few 10s thousands of tonnes to several hundred million tonnes, 0.1–10% REO e.g. Mt Weld: 12.24 million tonnes at 9.7% REO (up to 40% REO)	Mount Weld, Australia; Araxá, Brazil; Kangankunde, Malawi
Ion-adsorption clays	Residual clay deposits formed from the weathering of REE-enriched granites	>100	Most <10 000 tonnes, low-grade (0.03–0.35% REO)	Longnan, Xunwu, China

Table 3 Key characteristics and examples of the major REE deposit types. Specific deposits listed may fall into more than one mineral deposit class. Number of documented occurrences, compiled from Orris and Grauch (2002), with the exception of ion-adsorption clays (Grauch and Mariano, 2008), are indicative of the distribution of known deposits across deposit types. The grades and tonnages of deposits vary considerably within each deposit class.*

Notes:
(a) Includes igneous-affiliated, metamorphic, other fluorite and lead deposits of Orris and Grauch (2002).
(b) Fourteen placers of 'uncertain origin' are excluded.
(c) Classified as 'carbonatites with residual enrichment' by Orris and Grauch (2002).



REE mines	Other REE deposits/ occurences		
●	●	Carbonatite-associated	Primary deposits
●	●	Alkaline igneous rock-associated	
	●	Iron-REE deposits	
	●	Hydrothermal deposits exclusive alkaline settings	
○	○	Marine placers	Secondary deposits
	●	Alluvial placers	
	●	Paleoplacers	
	●	Lateritic deposits	
●	●	Ion-adsorption clays	

1 Mountain Pass, USA
2 Pajarito Mountain, USA
3 Gallinas Mountains, USA
4 Iron Hill, USA
5 Bald Mountain, USA
6 Bear Lodge, USA
7 Pea Ridge, USA
8 Green Cove Springs, USA
9 Carolina placers, USA
10 Lemhi Pass, USA
11 Snowbird, USA
12 Rock Canyon Creek, Canada
13 Hoidas Lake, Canada
14 Thor Lake, Canada
15 Elliot Lake, Canada
16 Strange Lake, Canada
17 Ilimaussaq complex, Greenland
18 Araxa, Brazil
19 Barro do Itapirapua, Brazil
20 Lovozero and Khibina complexes, Russia
21 Tamazeght complex, Morocco
22 Bou Naga, Mauritania
23 Nile Delta and Rosetta, Egypt
24 Etanero, Namibia
25 Okorusu, Namibia
26 Steenkampskraal, South Africa
27 Zandkopsdrift, South Africa
28 Plinesberg Complex, South Africa
29 Naboomspruit, South Africa
30 Palabora, South Africa
31 Richards Bay, South Africa
32 Kangankunde, Malawi
33 Congolone, Mozambique
34 Karonge, Burundi
35 Chavara, India
36 Amba Dongar, India
37 Orrisa, India
38 Perak, Malaysia
39 Maoniuping/Dalucao, China
40 Bayan Obo, China
41 Weishan, China,
42 Xunwu/Longnan, China
43 Dong Pao, Vietnam
44 Eneabba, Australia
45 Jangardup, Australia
46 Mount Weld, Australia
47 Brockman, Australia
48 Nolans Bore, Australia
49 Mary Kathleen, Australia
50 Olympic Dam, Australia
51 WIM 150, Australia
52 Dubbo Zirconia, Australia
53 Fraser Island, Australia

Figure 1 Map showing the global distribution of REE deposits.

Although rare, economic concentrations of REE-bearing minerals can be concentrated by primary crystallisation processes alone (Rankin, 2004). As a carbonatite body crystallises the majority of the REE are incorporated into apatite and calcite. During later cooling, calcite can be partially replaced by other minerals, releasing REE. These can be subsequently incorporated in monazite and other REE minerals such as bastnäsite and parisite as they crystallise from the fluids (Möller, 1986). The Mountain Pass deposit in California, USA is an important example of a deposit formed by magmatic processes. The Mountain Pass carbonatite is a moderately dipping, tabular Precambrian[19] intrusion into metamorphic rocks consisting of gneisses, granites and migmatites[20]. The carbonatites are associated with potassium-rich igneous rocks of a similar age. The REE minerals occur in veins, with the ore typically containing 10–15 per cent bastnäsite, 65 per cent calcite or dolomite and 20–25 per cent baryte. Sulphide minerals are rare in the ore, although galena is locally common (Evans, 1993; Castor and Hedrick, 2006; Castor, 2008a).

More commonly, REE deposits are also associated with late-stage vein and replacement mineralisation either within carbonatites or the surrounding host rocks. The fluids can be largely derived from the carbonatite or significantly post-date the intrusion, resulting from subsequent processes including metamorphism and/or weathering. Hydrothermal REE mineralisation typically takes the form of fracture and cavity fillings or fine-grained disseminations overprinting earlier formed minerals. Subsequent alteration and breakdown of primary minerals by lower temperature fluids may release REE which can potentially form secondary REE minerals (Wall and Mariano, 1996).

The Iron–REE–niobium deposit at Bayan Obo in Inner Mongolia, China is the world's largest REE deposit. The deposit is located on the northern margin of the North China craton, an extensional rifting environment in the mid-Proterozoic. The Bayan Obo deposit consists of three main ore bodies (Main, East and West) lying along an east–west-trending zone, more than 18 km in length. The deposits are stratabound[21] and hosted by mid-Proterozoic metasedimentary rocks of the Bayan Obo Group, largely within a dolomite marble (Wu, 2007). The mineralisation is thought to be largely Caledonian in age (420–555 Ma). Numerous carbonatite dykes are recognised in the district and several gabbros and alkali gabbros occur to the north and south of the ore bodies. Multiple mineralising stages are evident and over 170 minerals have been identified (Smith and Chengyu, 2000). REE principally occur as monazite and bastnäsite, although many other REE minerals are present including huanghoite, parisite and cebaite. REE-bearing niobium minerals are also common, the most widespread being colombite. The most important iron minerals are hematite and magnetite (Chao et al. 1997). The formation of the Bayan Obo deposit is the subject of considerable debate. Genetic models relating it to both carbonatite magmatism and hydrothermal iron oxide-copper-gold-(REE-uranium) mineralisation have been proposed. The origin of the dolomite hosting the deposit is disputed with some authors proposing a sedimentary origin whilst others suggest it is the result of carbonatite magmatism (Rankin, 2004). Recently published research concludes that carbonate minerals at Bayan Obo are derived from sedimentary carbonate rocks metasomatised by fluids likely to be derived from a carbonatite magma, enriched in REE (Yang. et al. 2009).

Less well known Chinese REE mineralisation, only identified in the 1990s, is associated with the Himalayan carbonatite-alkaline complexes of western Sichuan, south-west China. The deposits contain total reserves in excess of 3 million tonnes LREE and occur along a 270 km long zone, measuring 15 km wide. The largest deposit is Maoniuping, China's second largest REE resource, followed by Dulucao and a number of small- to medium-sized REE deposits and occurrences. The REE mineralisation is related to carbonatite sills and dykes and associated syenites[22]. Mineralisation is hosted in complex vein systems consisting of pegmatites, carbonatite breccias, stockwork[23] zones and disseminated mineralisation. The ores are dominated by baryte, fluorite, aegirine-augite, calcite and bastnäsite (Hou et al. 2009). The Maoniuping deposit formed during the Cenozoic[24] orogeny[25] and consists of a vein system extending for some 2.6 km. REE in the original carbonatite are thought to have been enriched by hydrothermal fluids (Wang et al. 2008). The deposit is estimated to contain 1.2 million tonnes of ore averaging 2.89% rare earth oxide (REO) (Hou et al. 2009).

The Lower Cretaceous[26] Chilwa Alkaline Province of southern Malawi lies at the southern end of the East

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[19] Precambrian: the period of time from the formation of the Earth, about 4500 million years ago to about 590 million years ago.

[20] Migmatite: a very high-grade metamorphic rock intermediate between metamorphic and igneous.

[21] Stratabound: an ore deposit that is confined to a single sedimentary bed or horizon.

[22] Syenite: a coarse-grained intrusive igneous rock consisting predominantly of potassium feldspar and little or no quartz.

[23] Stockwork: a network of many cross-cutting veins.

[24] Cenozoic: the period of geological time from 65 million years ago to present.

[25] Orogeny: a mountain building event resulting in folding and faulting of the Earth's crust.

[26] Cretaceous – a geological period from circa 145 to 65 million years ago.

African rift. It contains numerous mineralised carbonatitic and alkaline complexes, including the Kangankunde, Chilwa Island, Songwe and Tundulu complexes. Kangankunde is one of the largest carbonatites in the province and the richest in REE. It consists of approximately concentric zones of agglomerate, breccia, gneisses and fenite, surrounding a carbonatite core containing monazite, strontianite, fluorite and baryte. The monazite at Kungankunde is unusual for its high Ce levels and extremely low thorium and uranium content (Ministry of Energy and Mines, 2009). The REE-rich Okorusu fluorite deposit in northern Namibia developed from fluids expelled by the Cretaceous Okorusu carbonatite. A wide zone of brecciation and fenitization[27] surrounds the Okorusu complex. The fluorite mineralisation occurs at the outer edge of the zone of fenitization as either massive fluorite veins or replacement deposits (Buhn et al. 2002). The Amba Dongar Carbonatite complex in western India consists of a carbonatite ring dyke and a number of syenite intrusions, hosted in late-Cretaceous sandstones. Hydrothermal activity has resulted in REE enrichment of the carbonatites and associated fluorite mineralisation (Doroshkevich et al. 2009). The Early Cretaceous Barra do Itapirapuã carbonatites in southern Brazil are associated with REE mineralisation, resulting from hydrothermal overprinting of the original carbonatite. Hydrothermal alteration has resulted in the introduction of quartz, apatite, fluorite, REE fluorocarbonates, barytes and sulphide minerals. The REE were introduced during two stages of hydrothermal activity, probably related to magmatic fluids. The initial stage representing the peak REE-mineralisation deposited fluorocarbonates with quartz and apatite. A subsequent hydrothermal stage resulted in LREE depletion and HREE enrichment relative to the earlier mineralisation (Andrade et al. 1999; Ruberti et al. 2008).

Deposits associated with alkaline igneous rocks

Alkaline igneous rocks form from magmas so enriched in alkalis that they precipitate sodium- and potassium-bearing minerals (such as feldspathoids, alkali pyroxenes and amphiboles) not commonly found in other rock types. Alkaline igneous rocks vary widely in composition, from ultramafic[28] to felsic[29]. Alkaline rocks can be further classified as peralkaline if they have a higher molecular proportion of combined sodium and potassium than aluminium. Importantly peralkaline rocks are commonly characterised by extreme enrichment in alkaline metals, high-field strength elements[30] (HFSE) e.g. zirconium, titanium, yttrium, niobium and REE. REE deposits associated with peralkaline rocks are typically relatively low-grade, although, they are typically enriched in yttrium and HREE (Castor and Hedrick, 2006).

The formation of HFSE mineralisation in alkaline rocks is poorly understood. It is generally agreed that the initial enrichment of HFSE results from magmatic processes. In some instances magmatic processes are entirely responsible for the mineralisation, as is evident from deposits in which REE mineral-rich layers form part of a cumulate[31] sequence. In other examples hydrothermal processes have played the dominant role, upgrading initial magmatic concentrations. For example in the fluorspar associated REE deposits of the Gallinas Mountains in New Mexico, USA the total REE concentration in the quartz-syenite intrusion, the suggested source of the mineralising fluids, is ~650 ppm, compared to the deposit which grades 1.5–2.5 wt. per cent REE, requiring hydrothermal enrichment of around 25 times (Salvi and Williams-Jones, 2004). Fluorspar which commonly occurs in hydrothermal veins is a potential source of REE which substitute for calcium in fluorite or occur as associated REE minerals.

The Ilimaussaq alkaline complex in southern Greenland contains potentially exploitable deposits of REE, zirconium and niobium in eudialyte-rich cumulate layers. Twenty-nine separate eudialyte-rich layers have been defined, with a total resource of about 2 million tonnes, grading 1.5 per cent REO. The Khibina and Lovozero complexes on the Kola Peninsula, in Russia are some of the largest peralkaline igneous bodies in the world. The Khibina Complex hosts extensive nepheline syenite-associated apatite deposits thought to have crystallised from a magma. The apatite is enriched in yttrium amongst other elements. The Lovozero Complex is rich in zirconium, niobium, REE, yttrium, strontium, barium and phosphorus, which occur as eudialyte, loparite and apatite. Loparite has been mined periodically for about 50 years. Annual production is approximately 30 000 tonnes of loparite concentrate, containing 34 per cent REO (Salvi and Williams-Jones, 2004).

The Strange Lake Complex in eastern Canada consists of several HFSE-enriched peralkaline[32] plutons. The dominant

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[27] Fenitization – alkali chemical alteration of a rock resulting in enrichment in sodium and/or potassium.

[28] Ultramafic: composed chiefly of ferromagnesian (Fe-Mg) minerals, such as olivine and pyroxene.

[29] Felsic: a rock consisting chiefly of feldspars, feldspathoids, quartz, and other light-coloured minerals.

[30] High field strength element: elements which are not readily incorporated into the structures of common rock-forming silicate minerals during crystallisation of an igneous rock.

[31] Cumulate: igneous rocks or mineral-rich layers formed by the settling of crystals in a magma chamber.

[32] Peralkaline: igneous rocks with if they have a higher molecular proportion of combined sodium and potassium than aluminium.

REE-bearing mineral is gittinsite, but other important minerals include bastnäsite, monazite, kainosite, thorite and gadolinite. The Thor Lake deposit in the Northwest Territories of Canada is hosted in a syenite and associated alkaline granite. The larger of two deposits delineated contains 642 million tonnes of ore grading 1.96. per cent REE, amongst other elements. Other significant examples of REE enrichment associated with alkaline rocks include the Tamazeght Complex, Morocco, and the Pilanesberg Complex, South Africa (Salvi and Williams-Jones, 2004). The Weishan REE deposit in Shangdong Province, China consists of bastnäsite-barite-carbonate veins associated with syenite intrusions (Castor and Hedrick, 2006).

REE-bearing bastnäsite, Thor Lake. © Clint Cox, The Anchor House, Inc. 2007.

Deposits unrelated to alkaline igneous rocks

A diverse group of REE deposits are not obviously related to alkaline igneous rocks. The most significant group of these are the iron-REE deposits, also termed Olympic Dam-type or iron-oxide-copper-gold (IOCG) deposits. Notably REE concentrations are not a defining characteristic of these deposits as they are absent from many examples. They are hosted by a variety of rocks ranging from intrusive[33] igneous to volcanic and a variety of sedimentary rocks. In these deposits iron minerals (magnetite and hematite) form a significant component of the mineralisation. Copper sulphides are commonly present and other minerals include quartz, apatite, REE minerals (including bastnäsite, monazite, xenotime, allanite, parisite and apatite) uraninite and thorite. Deposits typically take the form of disseminated[34] to massive[35] replacement bodies, veins[36] and breccia zones. In deposits of this class the introduction of REE is commonly associated with two stages of mineralisation. In the early stage of deposit formation the REE occur in apatite associated with magnetite mineralisation. From an economic perspective this stage of mineralisation is less significant because of the generally low abundance of apatite, which typically has a low REE content. However, the second stage is considerably more important. In the case of the Olympic Dam deposit this mineralising stage consists of bastnäsite in association with hematite, quartz-sericite, bornite and baryte. Other REE-bearing minerals include florencite, monazite and xenotime (Samson and Wood, 2004). The massive Olympic Dam copper-uranium-silver-gold deposit in South Australia consists largely of a breccia-type ore containing up to 90 percent hematite. The ore is low-grade at around 0.5 per cent REO.

At the Pea Ridge iron deposit in Missouri, USA high-grade REE mineralisation is associated with breccia pipes related to a granitic body. The deposit contains monazite and xenotime, and is dominated by LREE, but also contains significant HREE enrichment. The extensive magnetite and hematite deposits at Kiruna, Sweden are reported to be enriched in REE (Castor and Hedrick, 2006). Some researchers include the huge Bayan Obo iron-REE-niobium deposit, China in the Olympic Dam class because of the abundant iron oxides (1.5 billion tonnes containing 35 per cent Fe) (Samson and Wood, 2004; Smith and Chengyu, 2000).

There are a number of REE deposits which do not display characteristics of the iron-REE deposits and are not obviously associated with alkaline or carbonatite intrusions. Examples include the REE mineralisation hosted in sedimentary rocks of the Rocky Mountains in North America. Fluorite associated REE mineralisation in sedimentary rocks occurs at Rock Canyon Creek in British Colombia, Canada and at the Snowbird deposit in Montana, USA. At Rock Canyon Creek mineralisation varies from finely disseminated to vein and breccia-hosted mineralisation associated with fluorite and baryte, REE minerals (synchysite and parisite dominate), quartz and carbonate. REE-thorium mineralisation occurs in sedimentary rock-hosted veins and breccia zones in the Lemhi Pass area along the Idaho-Montana border. The veins are rich in quartz, biotite and feldspar with hematite, monazite, thorite and apatite. The Hoidas Lake REE deposit in Saskatchewan, Canada is hosted by granitic[37] to dioritic[38], high-grade

[33] Intrusive: a body of igneous rock emplaced into pre-existing rocks.
[34] Disseminated: small, fine-grained particles of ore mineral dispersed through a rock.
[35] Massive: a homogenous structure.
[36] Vein: minerals deposited in fractures in a rock.
[37] Granite: an intrusive igneous rock dominated by quartz and feldspar.
[38] Diorite: an intrusive igneous rock dominated by plagioclase feldspar, hornblende, pyroxene and little or no quartz.

metamorphic rocks. The deposit is structurally controlled and lies close to a major fault zone. The mineralisation consists of a pyroxene- and apatite-rich vein system, containing allanite. The veins are controlled by north-east-trending faults forming a 60 metre wide mineralised zone, extending for nearly 500 metres (Harvey et al. 2002). In Australia, the Mary Kathleen uranium-REE skarn deposit consists of numerous lenses and veins of massive allanite and apatite, hosted in high-grade metasedimentary[39] rocks close to an alkali granite intrusion (Samson and Wood, 2004).

Secondary deposits

Placer deposits

Placer deposits are concentrations of resistant, heavy minerals transported and deposited with sand and gravel by rivers and/or coastal processes. These detrital minerals can originate from a diverse range of primary sources and frequently include minerals rich in titanium, zirconium and REE. The most important placer deposits containing significant quantities of REE minerals are Tertiary or Quaternary in age. However, deposits as old as Precambrian, known as paleoplacers are found in a few countries (Castor and Hedrick, 2006). Orris and Grauch (2002) identify more than 360 placer deposits world-wide. The most important REE-bearing mineral in placer deposits is monazite, with minor quantities of xenotime, fergusonite, euxenite, samarskite, allanite, knopite, pyrochlore and loparite (Möller, 1986). The most important placer deposits are of marine origin, developed along or in close proximity to current shorelines. The minerals in these deposits are concentrated by wave action, tides and currents. These heavy mineral deposits are largely exploited for their titanium and zirconium content. During the 1980s monazite and xenotime produced from titania-zircon beach placers in Australian were one of the most important sources of REE. Although historically important very little REE production is currently derived from monazite-bearing placers, owing to their typically high thorium content and associated high levels of radioactivity (Castor and Hedrick, 2006). Monazite typically forms a minor constituent of these deposits (typically less than 0.1 per cent) among the other heavy mineral phases and, as a result, REE production from placers was only economic because of the production of the other minerals. However, Australian deposits have local concentrations up to 1 per cent monazite and Indian ilmenite placer deposits can contain 1–2 per cent monazite (Möller, 1986).

Extensive heavy mineral sand placer deposits occur along the Australian coastline. Rutile-zircon-ilmenite deposits occur at Eneabba on the west coast, north of Perth. Historically these deposits annually produced about 2500 tonnes of monazite. The heavy mineral content of the sands at Eneabba is about 6 per cent, with a monazite content between 0.5–7 per cent. These deposits formed in the late Tertiary to early Pleistocene and are now located about 30 m above current sea level. The heavy minerals are thought to be derived from Achaean metamorphic rocks which were incorporated in Mesozoic sedimentary rocks before being reworked to form the placer deposits. Ilmenite-zircon, monazite-bearing placers of Pleistocene to Recent age are found in south-west Australia. Quaternary beach placers and sand dunes also occur along Australia's east coast. Current production is largely confined to rutile and zircon, with minor historical monazite production. Another important placer deposit in Australia, containing a large REE mineral resource, is located inland in the southern Murray Basin of Victoria. Here the WIM 150 deposit consists of a mid-Miocene, 14 metre thick sheet-like titanium and zirconium mineral sand body. Estimated reserves exceed 580 000 tonnes of monazite and 170 000 tonnes of xenotime (Castor and Hedrick, 2006; Whitehouse et al. 2000).

Monazite has been produced from placer deposits in a number of other countries. India has extensive beach sand deposits containing monazite in addition to other heavy minerals. The majority of the deposits occur along the present coastline and are estimated to contain 2.7 million tonnes of REO. In south-east Asia, monazite and xenotime occur in placer deposits worked for tin, zircon and titania. Alluvial tin deposits in Malaysia contain significant monazite and xenotime and Malaysia historically dominated yttrium production from xenotime. Monazite in addition to other heavy minerals was produced from Pleistocene marine sands at Green Cove Springs in Florida, USA. The USA has some historically important non-marine placer deposits. In these monazite typically occurs with ilmenite, zircon, magnetite and other minerals. Notable occurrences are the Carolina monazite belt and deposits in Idaho where monazite and euxenite were produced. (Gupta and Krishnamurthy, 2005; Castor and Hedrick, 2006).

A considerably older deposit containing REE-bearing minerals of possible placer origin occurs at Elliot Lake in Ontario, Canada. The deposit, formerly mined chiefly for uranium, consists of a metamorphosed early Proterozoic conglomerate containing REE in monazite, uraninite and brannerite. Metamorphism and hydrothermal activity may have subsequently enriched the heavy minerals (Castor, 2008b).

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[39] Metasedimentary: sedimentary rock that shows evidence of having been subjected to metamorphism.

Residual weathering deposits

Laterites are in situ residual deposits derived from prolonged tropical weathering which leads to the breakdown of many rock-forming minerals, leaching of certain elements (e.g. calcium and magnesium) and residual enrichment of less mobile elements (e.g. iron and aluminium). Under certain conditions and where the parent rock is enriched in REE, such as in carbonatites, REE may be enriched to form an economic deposit. Chemical weathering of carbonatites causes dissolution of calcite, dolomite and apatite. REE released from these minerals can be incorporated in new supergene[40] minerals, commonly phosphates including monazite. The deposits are typically high-grade, containing 10–25 per cent REO. The major REE deposit at Mount Weld, Western Australia is developed in a thick laterite, above a Proterozoic[41] carbonatite intrusion. The deposit has exceptionally high REO contents of up to 40 per cent occurring mainly in REE phosphate minerals. The unweathered carbonatite contains 0.1–0.2 per cent REO and the extreme enrichment is thought to result from leaching and redeposition of REE by groundwater over a sustained period (Lottermoser, 1990; Castor and Hedrick, 2006).

A number of Brazilian carbonatites display supergene enrichment of various mineral commodities associated with lateritic zones. The Cretaceous Araxá carbonatite in Brazil is a ring complex about 4.5 kilometres in diameter. Deep weathering has created a laterite rich in phosphorus, REE and niobium. The REE largely occur in secondary phosphate minerals (Pirajno, 2009; Castor and Hedrick, 2006).

A relatively newly recognised class of REE deposits are residual deposits of REE-bearing clays, termed ion-adsorption clays. These deposits associated with weathered REE-enriched granites occur throughout southern China, particularly in the provinces of Jiangxi, Guangdong, Hunan and Fujian (Grauch and Mariano, 2008). REE released during the weathering of the granites and the breakdown of primary minerals are absorbed by kaolin and other clay minerals such as halloysite. The weathered, REE-rich zones typically range from 3 to 10 metres thick and can be divided into four layers based on mineralogy: an upper layer dominated by soil (0–2 metres); a strongly weathered zone enriched in REE (5–10 metres), a semi-weathered layer (3–5 metres); and a weakly weathered zone with the same minerals as the original rock (Castor and Hedrick, 2006; Kanazawa and Kamitani, 2006). These are small deposits, in the range of 3000–12 000 tonnes, with low grades between 0.03–0.35 per cent total REO (Grauch and Mariano, 2008).

Extraction methods and processing

The diversity of REE-bearing deposits results in considerable variation in the mining and processing techniques used in their exploitation. Because REE are frequently exploited as by-products of other metals, these will frequently dictate the economics of the operation and the type of mining used.

Extraction methods

Surface mining

Surface mines are generally cheaper and safer to operate than underground mines. Open-pit mining is most appropriate for near-surface deposits, typically <100 metres, which are lower-grade, steeply dipping or massive ore bodies. This method typically involves removing the overburden, digging the ore or blasting with explosives, then removing the ore by truck or conveyor belt for stockpiling prior to further processing. Surface and underground mining are sometimes combined at a single mine, and may take place simultaneously in order to access shallow and deeper parts of an ore body. Hard rock deposits such as those containing bastnäsite are extracted using either open pit or underground methods. For example, the Bayan Obo deposit in China is mined from two large open pits using a standard open-pit mining approach (Jackson and Christiansen, 1993). The Mountain Pass deposit in California was also mined as an open pit, which was 150 metres deep. Blast holes were drilled at 3–4 metre spacing and assayed for REO using X-ray fluorescence (Castor and Hedrick, 2006).

Ion adsorption deposits, such as those found in southern China, are relatively low grade but mining and processing is simpler than for other types of deposit due to their near-surface, unconsolidated nature. The deposits are mined using open-pit methods. No drilling, blasting or milling is required considerably reducing extraction costs (Kanazawa and Kamitani, 2006).

Mining methods for placer deposits are dependent on whether they are submerged in water or on land. Dry mining operations use scrapers, bulldozers and loaders to collect and transport the typically poorly consolidated ore to the processing plant. Dry mining is suitable where deposits are shallow, contain hard bands of rock or occur in a series of discontinuous ore bodies (Iluka, 2010). Drilling and blasting is not generally required except in limited areas where the sand has been cemented by ferruginous or calcareous precipitates (Jackson and Christiansen, 1993). When placer deposits

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[40] Supergene: near-surface processes of leaching and transportation of metals followed by re-precipitation.

[41] Proterozoic: the period of geological time extending from 2500–542 million years ago.

are submerged in water or are affected by a high water table, extraction typically uses a dredger. Dredgers are floating vessels which either use a series of buckets or a suction device to recover material from the base of the water column. Dredgers are also used in artificial ponds, pumping ore in slurry form to a floating concentrator (Iluka, 2010).

Placer deposit mining © image courtesy of Iluka Resources

Underground mining

Underground extraction uses a variety of standard mining methods depending on the characteristics of the ore body. Typically, these operations use labour-intensive drilling and blasting techniques, though attempts are being made to introduce more mechanisation into the workplace. Room and pillar is an underground mining method where mining progresses in a near horizontal direction by opening multiple stopes or rooms leaving pillars of solid material for roof support. Ore is blasted using explosives then transported to the shaft using an underground rail system. Old workings may be backfilled with waste material to improve ventilation by forcing air to travel through only those areas that are being worked, as well as providing more roof support. Underground room and pillar methods were used at the Elliot Lake, mine in Canada where REE were extracted as a by-product of uranium production (Harben, 2002). Loparite from the Lovozero complex in Russia is mined using both underground and open pit methods (Castor and Hedrick, 2006).

By-product production

REE are very rarely mined as the only or primary product of a mine. Mountain Pass in California is the only mine which has operated exclusively for the recovery of REE. REE were originally extracted from Bayan Obo in China as a by-product of iron ore extraction. Loparite production in Russia was a by-product of titanium extraction and REE have been recovered from uranium mining operations in Canada. The Dubbo Zirconia operation in Australia will produce REE in addition to zirconium and niobium. REE in mineral sand deposits are generally by-products of titanium, zircon or tin extraction. Brazil is the only country where a mineral sand deposit has been worked exclusively for monazite. However, this was principally for the thorium content rather than the REE. Deposits such as Mount Weld in Australia have the potential to be exploited purely for their REE content (Gupta and Krishnamurthy, 2005).

Processing

After mining the ores are processed to increase their REE content. Concentration is normally undertaken at, or close to, the mine site and involves crushing the ore and separating REE and gangue minerals, using a range of physical and chemical processes.

Physical beneficiation

Hard rock deposits

Following mining bastnäsite ore is crushed and screened. At the Mountain Pass deposit in California the crushed ore was deposited in layers to form blending piles containing an average of seven per cent REE oxide. This material was subsequently sent to the mill's fine ore bin and conveyed to a ball mill where the particle size was reduced to approximately 0.1 mm. The material then underwent up to six conditioning treatments with steam and different reagents being added at each stage to produce a slurry containing 30–35 per cent solids. The slurry was processed by flotation to produce a bastnäsite concentrate (Figure 2). Froth flotation[42] is a selective process for separating minerals using water, chemicals and compressed air. Following grinding, water is added to the powdered ore to produce a suspension[43]. Air is blown upwards through the tanks. Chemicals are added which make specific minerals water repellent and cause air bubbles to stick to their surfaces. Consequently, these minerals collect in a froth at the surface and are removed. Reagents[44] used for monazite flotation include fatty acids, hydroxamates[45] and dicarboxylic[46] acids. However, there are problems with flotation separation as some of the common gangue minerals associated with bastnäsite, such as baryte and calcite, have similar flotation properties (Gupta and Krishnamurthy, 2005).

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[42] Froth flotation: a process for selectively separating hydrophobic (lacking affinity for water) materials from hydrophilic (having a strong affinity for water).

[43] Suspension: a mixture in which fine particles are suspended in a fluid where they are supported by buoyancy.

[44] Reagent: a substance or compound that is added to a system in order to bring about a chemical reaction.

[45] Hydroxamate: a hydroxylamine (a reactive chemical with formula NH_2OH) compound containing a CONOH group.

[46] Dicarboxylic acid: organic compounds that are substituted with two carboxyl functional groups (a carboxyl functional group consists of a carbon atom joined to an oxygen atom by a double bond and to a hydroxyl group, OH, by a single bond).

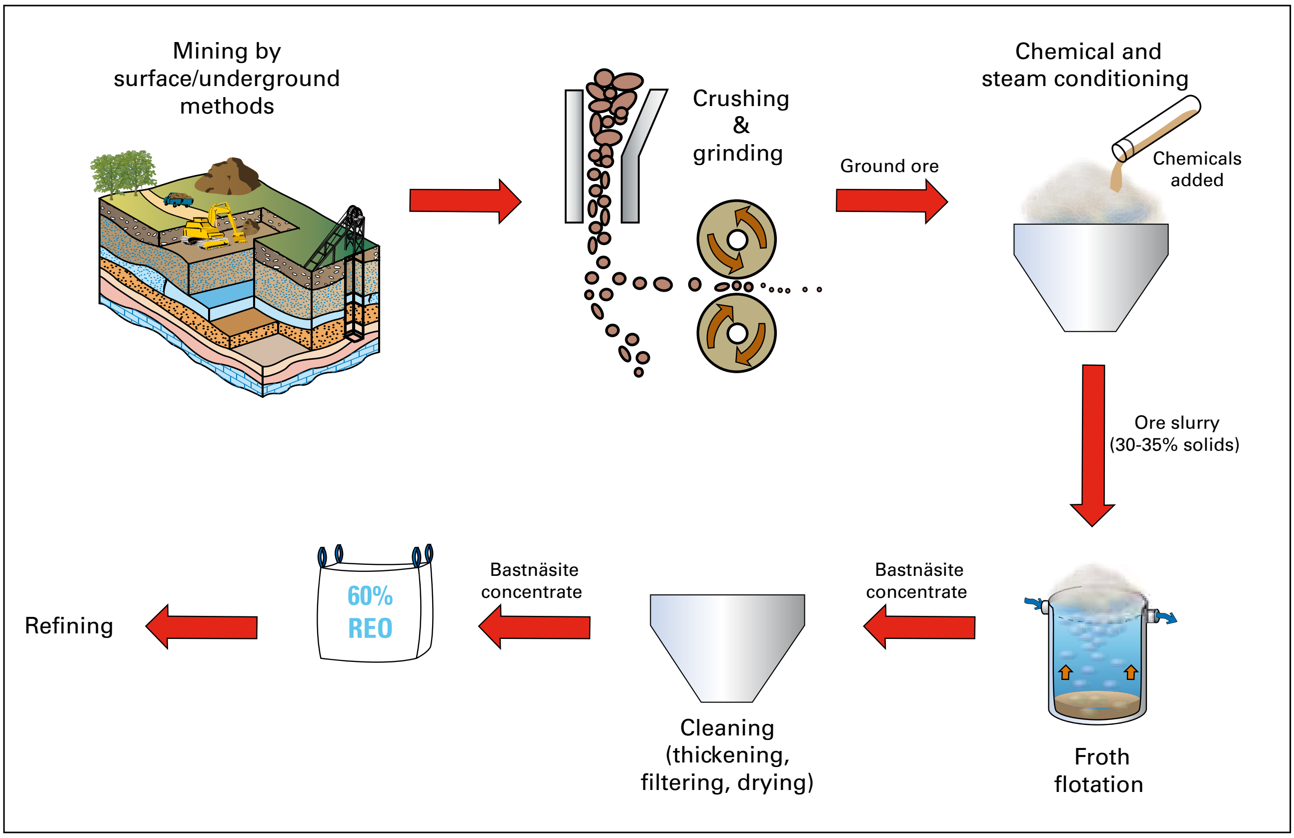

Figure 2 Generalised bastnäsite beneficiation flow diagram, based upon the Mountain Pass operation.

Following flotation the ore is cleaned. At Mountain Pass a four stage cleaning method was devised producing a final concentrate of 60 per cent REE oxide with an overall recovery of 65 to 70 per cent (Gupta and Krishnamurthy, 2005).

Mountain Pass is unusual in that REE are the only product from the mine. Other operations generally produce REE as a by-product of other minerals and accordingly the beneficiation methods vary greatly. For example at the Bayan Obo deposit magnetite, hematite, fluorite and niobium oxide are also recovered so the beneficiation process is influenced by this requirement (Castor and Hedrick, 2006). The iron ore is separated by flotation and a bastnäsite concentrate and a mixed bastnäsite -monazite concentrate are produced (McKetta, 1994). Physical beneficiation of loparite in Russia uses a combination of gravity and electrostatic methods to produce a 95 per cent loparite concentrate (Castor and Hedrick, 2006).

Placer deposits

Since placer deposits show considerable variation in mineralogy and chemical composition the beneficiation methods vary greatly. In many cases gravity separation is used as it is particularly effective for separating minerals with significant differences in densities. The sediment is fed into a suspension, and the gangue particles, having a lower density, tend to float and are removed as waste. The higher density minerals of economic value sink and are also removed. Equipment including jigs, spiral and cone concentrators and shaking tables are used in gravity separation (Castor and Hedrick, 2006). In placer deposits the initial gravity separation is completed on the dredge during mining and unwanted tailings are discharged back into previously mined areas (McKetta, 1994). Higher grade deposits such as the Chavra and Manavalakurichi sands in India contain 70–80 per cent heavy minerals and do not require this pre-concentrating stage (Gupta and Krishnamurthy, 2005).

The concentrate produced by gravity concentration is processed in a dry mill. Concentrates of ilmenite, rutile, leucoxene, zircon and monazite are produced using a combination of gravity, magnetic and electrostatic methods (Figure 3). Monazite, in contrast to ilmenite, rutile and many other heavy minerals found in placer deposits, is non-conductive and is separated, with zircon, by electrostatic methods. It is then separated from the zircon by electromagnetics or further gravity methods as it is moderately susceptible to magnetism and has a higher density. Xenotime is usually separated from monazite using precise gravity methods as they have very similar density and magnetic properties (McKetta, 1994). For finer grained deposits (between 15 and 100 microns) gravity separation is not an efficient method so flotation is used (Gupta and Krishnamurthy, 2005).

Chemical beneficiation

Following physical beneficiation to produce a REE mineral concentrate subsequent processing is required to extract the REE (Figure 4). The processes used for this have not developed considerably over the last 20 years and the processing route selected depends on the type of minerals and the economics of the operation (Chegwidden and Kingsnorth, 2002).

Hard rock deposits

At the Mountain Pass deposit the bastnäsite concentrate (about 60% REO) obtained from physical beneficiation was upgraded to about 70 per cent by leaching with hydrochloric acid to remove strontium and calcium carbonates. Calcination was then used to remove the carbon dioxide leaving an 85–90% REO concentrate (Jackson and Christiansen, 1993). At Bayan Obo the mineral concentrate is baked with sulphuric acid at 300–600°C and leached with water, taking the REE into solution and precipitating other elements as waste (liquid-solid separation). The REE are then precipitated as double sulphates, converted to hydroxides and leached with hydrochloric acid for purification. Loparite concentrate in Russia is processed using gaseous chlorination at high temperatures in the presence of reducing agents. Titanium, niobium and tantalum are separated from REE chlorides and other elements which remain as a fusion cake. This cake is then dissolved in sulphuric acid in the presence of ammonium sulphate. Water is added to dilute the solution and sodium carbonate is used to precipitate the REE and thorium (Castor and Hedrick, 2006).

Unconsolidated deposits

REE extraction from monazite and xenotime involves dissolution of the minerals in hot concentrated alkaline (caustic soda method) or acidic solutions (acid treatment). Acid treatment uses hot sulphuric acid digestion then leaching with water to remove the phosphate content. A dilution stage follows whereby a process of selective precipitation deposits thorium and REE as double sulphates (Castor and Hedrick, 2006). The sulphuric acid method has been used on a commercial basis in the past but it is no longer in use as it does not yield a pure product (Gupta and

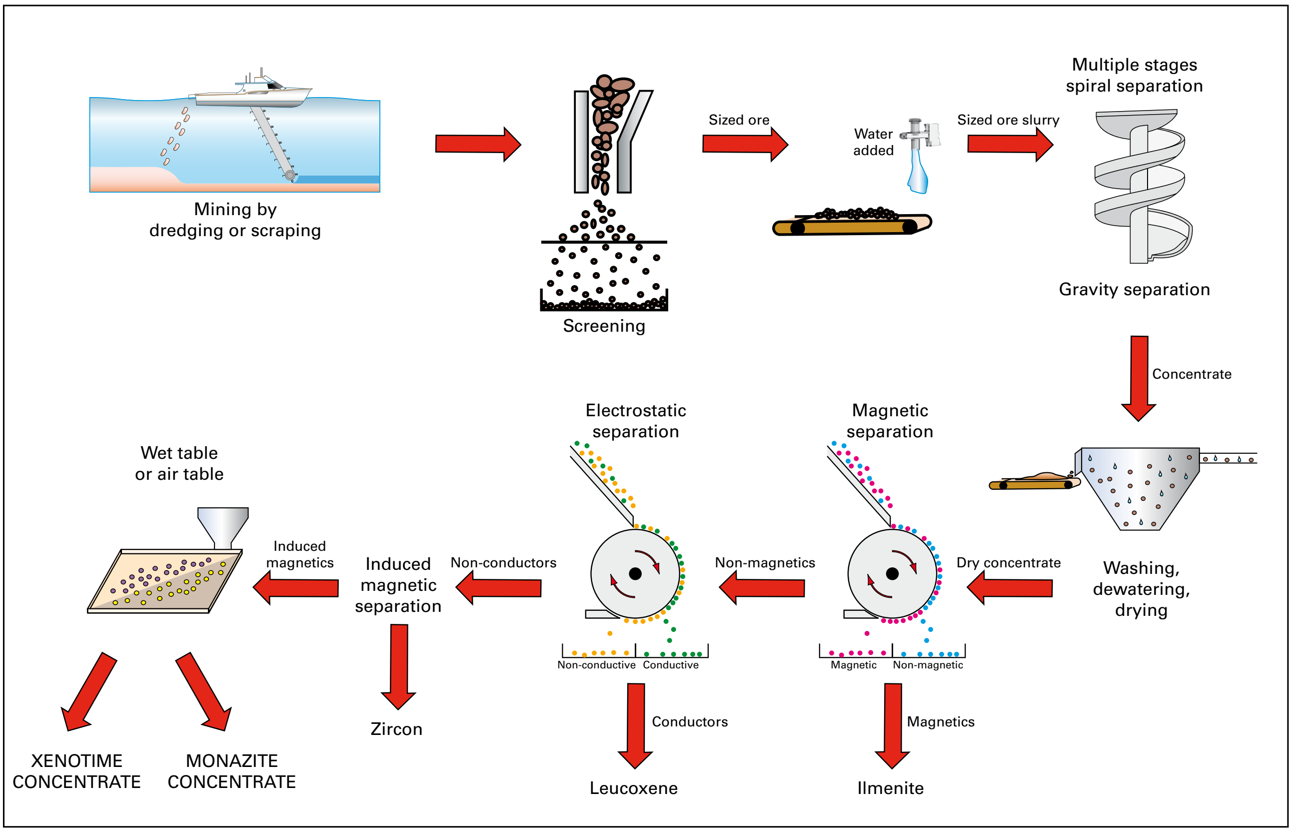

Figure 3 Generalised flow diagram for extraction of monazite and xenotime from placer deposits.

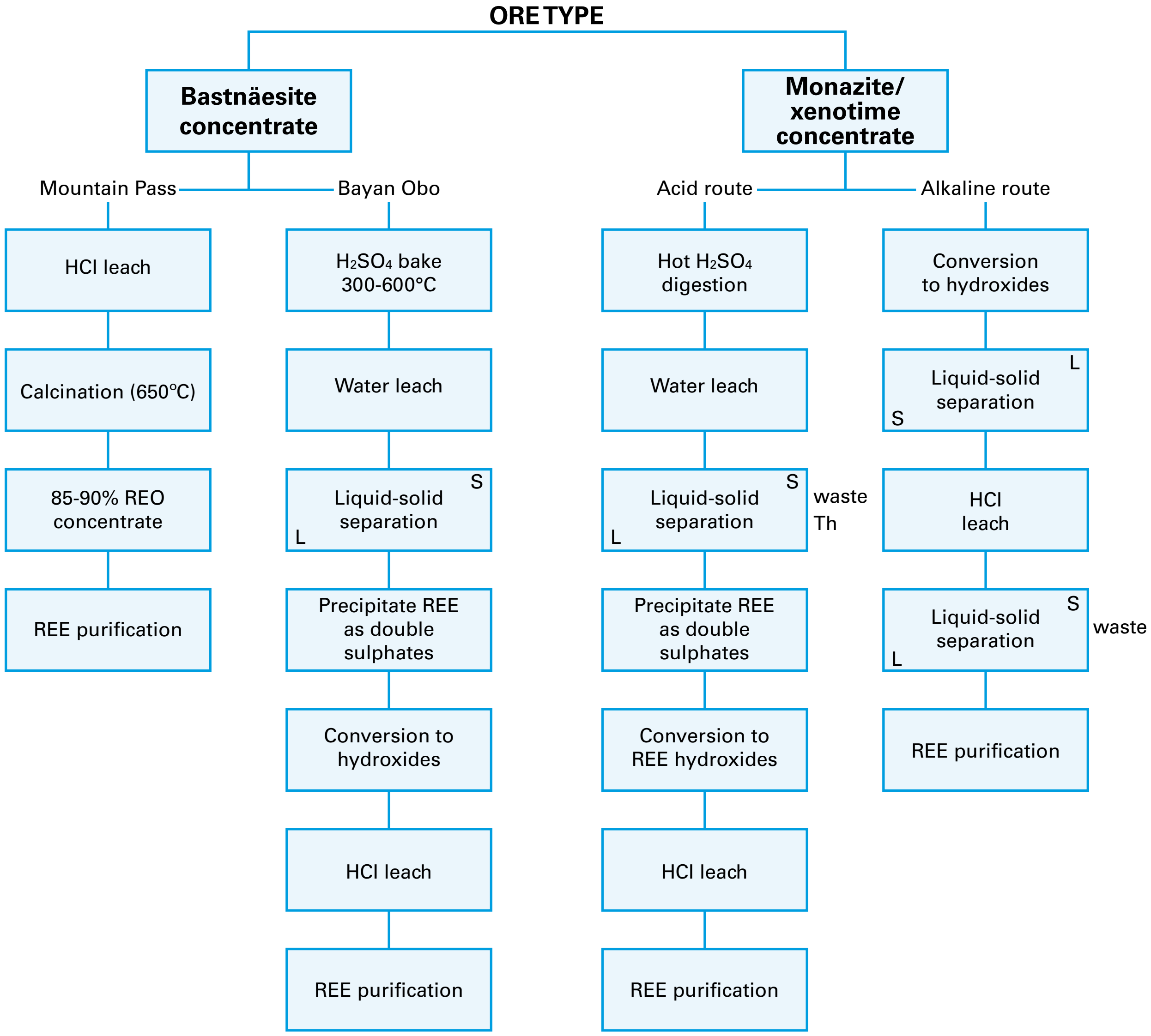

Figure 4 Examples of chemical processing routes for the major REE-bearing minerals. H_2SO_4, sulphuric acid; HCl, hydrochloric acid (adapted from Chegwidden and Kingsnorth, 2002).

Krishnamurthy, 2005).The caustic soda method involves dissolution of the minerals in a concentrated solution of sodium hydroxide, at 140–150°C, converting the REE and thorium to hydroxides. The phosphate compound is separated by dissolving in water and recovered as trisodium phosphate. REE are separated from thorium using partial dissolution in which REE are dissolved in concentrated hydrochloric acid whilst the undissolved material is filtered and forms thorium cake waste (Gupta and Krishnamurthy, 2005). The caustic soda method is used in India by Indian Rare Earths Ltd and was used in Malaysia at the Asian Rare Earth (ARE) plant until its closure in 1994 (Meor Yusoff and Latifah, 2002). This is the preferred process for chemical treatment as the phosphate can be recovered as a marketable by-product, whereas with acid treatment the phosphate is lost (Gupta and Krishnamurthy, 2005).

Processing of ion adsorption clays is relatively straight forward compared with other types of REE deposit as they do not require the processing of complex minerals that characterise hard rock deposits. A simple leaching process produces a solution containing REE from which a concentrate can be precipitated (Molycorp, 1993). This simple procedure means these types of deposits can be economically exploited despite their relatively low grades (0.03 to 0.35% total REO) (Grauch and Mariano, 2008). Additional benefits include their low contents of cerium and radioactive minerals, and their enrichment in HREE and yttrium.

Separation of individual REE

The high value of REE depends on their effective separation into high purity compounds. Separating individual REE from concentrates is a very difficult process due to their similar chemical properties (Morais and

Ciminelli, 2004). REE processing is most advanced in China, which can supply REE products at 99.9999 per cent purity, whilst French companies typically produce 99.99 per cent pure REE and Japanese sources 99.9 per cent REE (Zhongde, 2009).

Selective oxidation or reduction of certain REE can be useful in the separation process. In general REE are characteristically trivalent[47] but cerium, praseodymium and terbium can occur in the tetravalent[48] state as well as the trivalent state and samarium, europium and terbium display divalency[49]. These differences in chemical behaviour can be exploited in the separation of individual elements (Gupta and Krishnamurthy, 2005). Cerium and europium are generally separated by selective oxidation whilst other REE can be separated using fractional crystallisation[50], fractional precipitation[51], solvent extraction and ion exchange methods. These methods are based on the small differences in basicity[52], resulting from decreasing size in ionic radius from lanthanum to lutetium (Morais and Ciminelli, 2004). Until the early 1950s fractional precipitation and fractional crystallisation were the only techniques available for separating REE. These processes, however, are laborious and inefficient and have consequently been superseded by more effective techniques like ion exchange and solvent extraction (Gupta and Krishnamurthy, 2005). The solvent extraction method is most appropriate for separating the LREE, with the HREE being more difficult to extract using this method (Moore, 2000).

Ion exchange is a process in which ions are exchanged between a solution and an insoluble (usually resinous) solid. The solution containing the REE is then passed over the ion exchange resin. The REE displace the cations[53] on the resin surface. This produces an aqueous waste containing the exchanged cations, with a mixture of REE deposited on the resin. Individual REE are then separated using a complexing agent which has different affinities for the various REE (EPA, 2008). The ion exchange method produces highly pure REE in small quantities. However, it is a time consuming process and only a few HREE are purified commercially on a small scale using ion exchange. For large scale production solvent extraction is the preferred route (Molycorp, 1993).

Solvent extraction (SX), or liquid-liquid extraction, is a method used to separate compounds on the basis of their relative solubilities in two immiscible[54] liquids, typically water and an organic solvent. This process relies on differences in the relative solubilities of REE in the liquid phases used.

On an industrial scale the SX process is carried out in a group of mixer settlers, called batteries. This allows repetitive fractionation during a continuously flowing process. Initially the process is relatively ineffective as the chemical properties of the REE ions in solution show only incremental variation with atomic number. However, when the process is repeated many times each REE is successfully separated from the others (Rhodia, 2009; Uda et al., 2000).

The end products of SX are usually solid-rare earth salts or oxides. An insoluble salt is precipitated from the solution obtained from the solvent extraction process. This is separated, dried or calcined at high temperatures and then ground (Rhodia, 2009). REE compounds with a purity of more than 99.99 per cent can be produced using this method (Castor and Hedrick, 2006).

Environmental implications

There are many environmental issues associated with REE production. These commonly result from insufficient environmental regulations and controls in the areas where REE are mined and processed. One of the most significant relates to the radioactivity of some ores. For example xenotime in Malaysian placer deposits typically contains 2% uranium and 0.7% thorium. This was the main reason that the Malaysian processing industry failed and the plants were closed (Meor Yusoff and Latifah, 2002). Processing of beach sands containing monazite has been banned in Australia, China and Europe due to environmental concerns (Curtis, 2009).

A major advantage of the ion adsorption clay deposits in southern China is their low radioactive element content (Kanazawa and Kamitani, 2006). However, significant environmental issues are associated with exploiting these deposits due chiefly to their

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[47] Trivalent: Having a valance of three.

[48] Tetravalent: Having a valence of four.

[49] Divalency: Having a valance of two (valency is a measure of the number of chemical bonds formed by the atoms of a given element).

[50] Fractional crystallisation: the process of separating the components of a solution on the basis of their different solubilities, by means of evaporating the solution until the least soluble component crystallises out.

[51] Fractional precipitation: removal of some ions from solution by precipitation while leaving other ions with similar properties in solution.

[52] Basicity: The degree to which a substance is basic or alkali.

[53] Cation: a positively charged ion.

[54] Immiscible: one (or more) liquids that are unmixable or insoluble with each other.

illegal status and lack of adherence to environmental regulation. However, even the regulated mines in southern China, as well as the mines working bastnäsite deposits in Batou, still pose significant hazards because of the chemicals used in processing. Reports indicate that the chemicals used in the refining process have been responsible for disease and occupational poisoning of local residents, water pollution and destruction of farmland (Hilsum, 2009). It has been reported that refining one tonne of REE oxide can potentially produce 60 000 m^3 of waste gas containing sulphuric and hydrofluoric acid, 200 m^3 of acidic water and 1.4 tonnes of radioactive waste (China Daily, 2010). It is suggested that the limited regulatory controls on China's REE industry has resulted in reduced costs to producers, contributing to its dominance of the market. However, there are indications that China is becoming increasingly aware of the environmental impacts of REE production. It has closed eighty REE production facilities in an attempt improve efficiency and environmental performance, which is likely to impact on global supplies (Williams, 2009). In addition the Batou Institute of Rare Earths, the world's largest research institute for the industry, is undertaking seven projects aiming to make refining technology more efficient and less environmentally damaging (China Daily, 2010).

As with all extractive operations, REE production uses a considerable amount of energy, and in China most of which is supplied by coal-fired power stations. With increasing concerns about climate change and carbon emissions this may prove to be a significant factor influencing REE production.

Conversely REE products are increasingly used in environmental applications as they offer improvements in energy efficiency and can reduce carbon dioxide emissions. For example, using lanthanum in rechargeable batteries instead of nickel-cadmium, results in fewer environmental problems as, unlike most other types of rechargeable batteries, they do not contain cadmium or lead (Haxel et al., 2002). Use of REE in fluorescent lamps and gadolinium and thulium in magnetic refrigeration significantly reduce carbon dioxide emissions due to increased energy efficiency (Turner et al., 2007).

Specifications and uses

REE have been traded in a wide variety of forms since they were first exploited. Over the last 40 years the form of Chinese REE exports has changed considerably. In the 1970s exports were largely mineral concentrates, changing in the 1980s to predominantly mixed REE chemicals such as carbonates and chlorides. By the early 1990s separated REE oxides and metals were in greater demand, but by the end of the decade trade was dominated by REE magnets, phosphors and polishing powders. In the 2000s there is considerable trade in components and products containing REE such as magnets, computer hard drives, electric motors and liquid crystal displays (LCDs) (Kingsnorth, 2008a).

Specifications for REE mineral concentrates, compounds and metals vary depending on their end-use. Advances in processing techniques have removed the markets for lower specification products, for example a 90 per cent cerium oxide product used in the glass industry has been replaced by higher-grade cerium products with little or no price penalty (Castor and Hedrick, 2006).

REE are used in the widest range of consumer products of any group of elements (Castor and Hedrick, 2006). REE are indispensable in electronic, optical, magnetic and catalytic applications (Figures 5–7). In these applications REE play a vital role in environmental protection, improving energy efficiency and enabling digital technology, making them critical in a rapidly growing and developing world.

Catalysts

Catalysts[55] accounts for a significant share of the REE market by volume (19 per cent), but only five per cent of the total market value (Kingsnorth, 2009). REE are essential in automotive catalytic converters, which transform the primary pollutants in engine exhaust gases into non-toxic compounds. Cerium carbonate and cerium oxide are used in the catalyst substrate and as a component of the converter's oxidising catalyst system (Castor and Hedrick, 2006). The REE play a critical role in the chemical reactions within the autocatalyst and also enable it to run at high temperatures. They also increase the effectiveness and reduce the amount of platinum and other precious metals required, thereby decreasing costs (Lynas, 2010).

REE are also important in fluid cracking catalysts[56] which are used in the process of refining crude oil, transforming the heavy molecules into lighter compounds that make up petrol and other fuels such as gas, jet fuel and diesel. Lanthanum and cerium are used to stabilise the structure and chemistry of the high surface area zeolites used as a molecular filter in this application (Lynas, 2010).

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[55] Catalyst: a substance that initiates or accelerates a chemical reaction without itself being affected.

[56] Fluid cracking catalyst: catalyst used in the transformation of heavy molecules into lighter compounds.

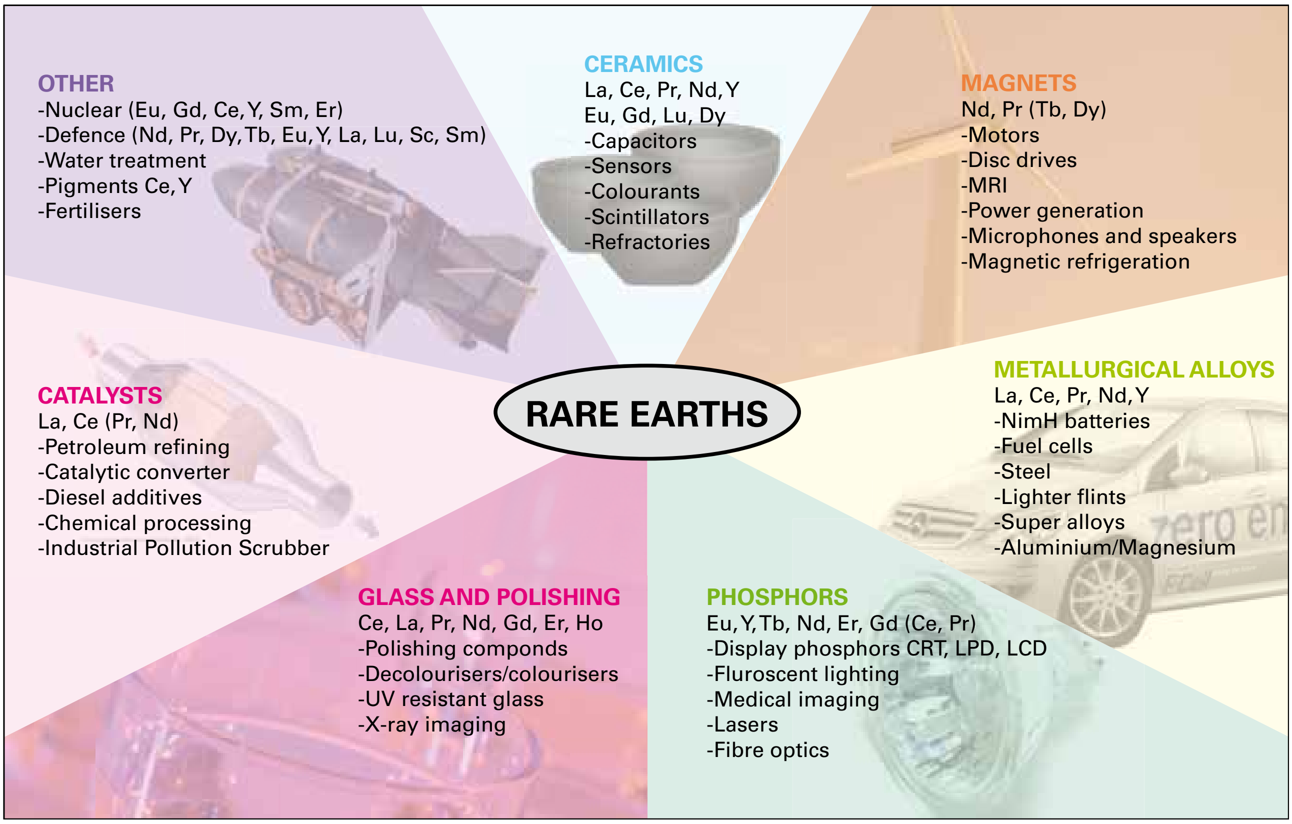

Figure 5 Applications of rare earths. Images courtesy of Johnson Matthey Plc, Mercedes-Benz and Ingrey Publishing.

Magnets

An increasingly important use of REE is in permanent magnets. This application was first developed in the 1960s when samarium alloyed with cobalt was used. By the mid 1980s neodymium–iron–boron magnets had been developed and have now largely replaced samarium–cobalt magnets, except in high temperature applications (Castor and Hedrick, 2006). Neodymium–iron–boron magnets posses a magnetic energy of up to 2.5 times greater than the samarium-cobalt versions. In addition the principal constituent is iron (84.4 per cent) which is significantly cheaper and more abundant than cobalt (Gupta and Krishnamurthy, 2005). Permanent magnets account for approximately 38 per cent of the REE market by value and 21 per cent by volume.

Because neodymium magnets are more powerful than alternatives, they provide improved performance for a smaller size which has lead to many miniaturised applications. Tiny neodymium magnets are used in the speakers in earphones for consumer devices such as MP3 players, as well as in numerous other high performance speakers. This results in smaller, lighter devices with improved performance. Permanent magnets are also used in hard disk- and DVD-drives. The voice coil motor which controls the arm that reads and writes information onto the disk uses a neodymium-based magnet which gives improved control allowing thinner tracks and more data storage (Lynas, 2010).

Neodymium–iron–boron magnets are important in many ‘green’, carbon reducing technologies. It is estimated that wind turbines use in the range of 0.6–1.0 tonne of neodymium magnets per megawatt, of which approximately 30 per cent is REE (Avalon Rare Metals, 2010; Lifton, 2009a). In wind turbines electricity is generated in an alternator when magnets pass wire coils. One factor which determines the amount of electricity generated is the strength of the magnets used. The stronger the magnets, the higher the current generated, so strong neodymium magnets make considerably better alternators (Reuk, 2007).

Neodymium magnets are essential for hybrid cars such as the Toyota Prius. Hybrid cars reduce fossil fuel consumption by combining a petrol engine, battery-powered electric motors and brakes that capture energy during breaking (Avalon Rare Metals, 2010). It has been suggested that the Prius is the largest consumer of REE of any individual product with each electric motor in a Prius requiring one kilogram of neodymium (Lifton, 2009b).

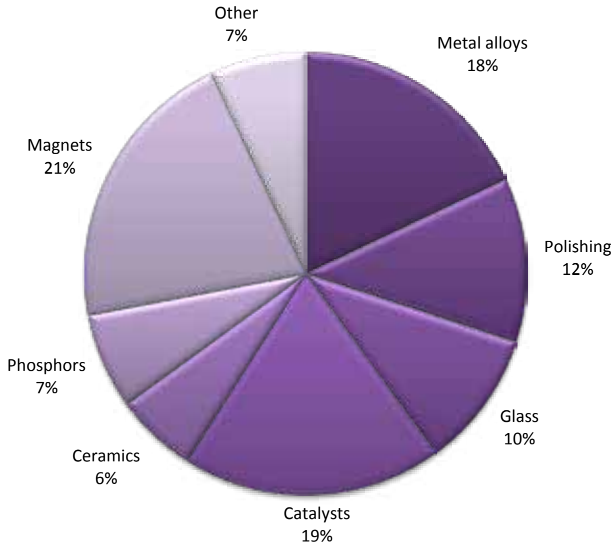

Figure 6 REE consumption by volume (Kingsnorth, 2009).

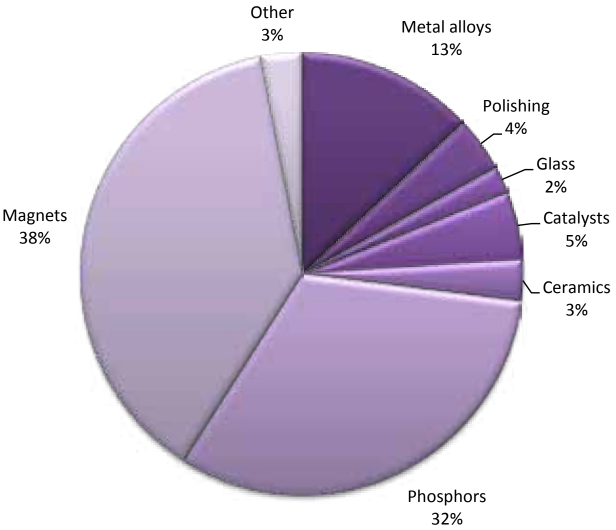

Figure 7 REE consumption by value (Kingsnorth, 2009).

The use of REE magnets has the potential to increase the energy efficiency of many appliances. For example use of REE magnets in air conditioning systems can reduce power consumption by up to 50 per cent whilst retaining the same level of performance (London, 2009). Dysprosium and terbium are also used in magnets. Many magnets tend to lose their magnetism as they heat up, but the addition of dysprosium or terbium prevents this from happening at high temperatures (Venter, 2009).

Metallurgical alloys

REE have major applications in metallurgical alloys. In 2008 this use accounted for 18 per cent of global consumption by volume (Kingsnorth, 2008a). One of the oldest uses of REE as an alloy is in mischmetal, a pyrophoric[57] alloy containing only REE metals. The individual REE are present in the same proportions as they naturally occur in the bastnäsite concentrates (Gupta and Krishnamurthy, 2005). Typical composition is about 50 percent cerium and 25 per cent lanthanum with small amounts of neodymium and praseodymium. The most common use of this alloy is in the flint ignition device of many lighters and torches, although for this purpose it is blended with iron oxide and magnesium oxide since the REE alloy alone is too soft (Venter, 2009). Mischmetal and cerium are commonly used as minor alloying additives for controlling inclusions in cast irons and steels. The cerium combines with the sulphide inclusions to form more rounded particles which are less likely to promote cracking (Lundin and Wilson, 2009).

Wind turbine © BGS NERC.

Superalloys are a class of heat resistant alloys used in applications involving intense, high-temperature oxidising environments such as in gas turbine engines and electric generators. Adding REE enhances the alloy's oxidation resistance. In M–chromium–aluminium–yttrium alloys (where M is iron, nickel or cobalt), yttrium is the active component but lanthanum and cerium are also used in certain nickel and cobalt superalloy compositions.

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[57] Pyrophoric: a material which can spontaneously ignite in air.

Less than one per cent of REE metal in a superalloy can dramatically improve its performance (Gupta and Krishnamurthy, 2005).

The use of REE as a method of storing hydrogen was identified in 1969 when it was discovered that the intermetallics[58] REM5 (where RE is the rare earth and M is iron, cobalt or nickel) could absorb a large amount of hydrogen at room temperature. Solid state storage of hydrogen is better than storage as cryogenic[59] and compressed gas in terms of safety, volume, weight, pressure and energy savings (Gupta and Krishnamurthy, 2005).

REE are used in nickel metal hydride (NiMH) rechargeable batteries that power many electronic products. A mixed rare earth metal alloy is used as the anode in the NiMH battery, representing about 26 per cent of the battery's weight. Lanthanum is the main REE used in the NiMH battery (Australian Rare Earths, 2010). These batteries in addition to many other REE-bearing components, are particularly important for hybrid cars such as the Toyota Prius (Figure 8). It has been calculated that each Toyota Prius battery uses 10 to 15 kg of lanthanum (Lifton, 2009b).

Phosphors

REE are commonly used in phosphors[60]. This application accounted for 32 per cent of global consumption by value in 2008, although only seven per cent by volume (Kingsnorth, 2009). Phosphors are important in televisions, computer screens and any other visual display devices that requires cathode ray tube, liquid crystal display or plasma display panel technologies (GWMG, 2010). The colours seen on the display come from the use of europium–yttrium compounds for red, terbium–fluoride–zinc sulphide for green and cerium–strontium–sulphide for blue. These phosphors emit luminescence[61] when activated by photons[62] (Jackson and Christiansen, 1993). Plasma screens were developed with the aid of a new europium-based blue phosphor which retains brightness ten times longer than previous blue phosphors (Lynas, 2010).

Energy efficient lighting is a major application of REE phosphors. The compact fluorescent lamp (CFL) uses only a quarter of the power needed to produce the same amount of light as the standard incandescent light bulb (Lynas, 2010). More recently REE phosphors are being used for white LEDs. LEDs are 80 per cent more efficient than incandescent lighting, and 40 per cent more efficient than compact fluorescent bulbs (Avalon Rare Metals, 2010). REE are used in the manufacture of fibre optics and lasers. In lasers REE, typically neodymium, are used as an activator. Glass fibres containing REE can transmit data over exceptionally large distances without booster stations (Jackson and Christiansen, 1993). REE lasers are being increasingly used for medical and dentistry applications. This is one of the major applications for erbium. Erbium lasers are used in cosmetic treatments to ablate[63] the epidermis[64] revealing the smoother and younger looking underlying skin. In dentistry, the erbium lasers have proven safe and effective for the removal of tooth decay and cavity preparation in addition to many soft-tissue and

Figure 8 REE applications in a hybrid electric vehicle © Molycorp Inc. 2010.

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[58] Intermetallic: solid state phases involving metals.

[59] Cryogenic gas: a gas that has been liquefied by lowering the temperature, usually to a temperature under about -100°C.

[60] Phosphor: a substance that exhibits the phenomenon of phosphorescence (sustained glowing after exposure to energized particles such as electrons or ultraviolet photons).

[61] Luminescence: any process in which energy is emitted from a material at a different wavelength from that at which it is absorbed.

[62] Photon: discrete bundle (or quantum) of electromagnetic (or light) energy.

[63] Ablate: elimination of tissue from the body.

[64] Epidermis: the thin, outermost layer of skin.

hard-tissue surgical procedures (Margolis, 2006).

Glass and polishing

REE are commonly used in the glass industry. Glass and polishing applications accounted for 22 per cent of total REE consumption by volume in 2008, although only six per cent by value (Kingsnorth, 2009). The earliest commercial use of cerium was in 1896 when it was first used as a decolourising agent in glass. Decolourising is necessary as iron oxide is always present as an impurity in glass causing a yellow–green colour. Adding cerium oxidises the iron (Jackson and Christiansen, 1993). REE are also used as dyes in glass. Small amounts of cerium will decolourise glass but about one per cent will turn it yellow and larger quantities brown. Neodymium colours glass red, praseodymium green and holmium blue. Erbium is used to colour glass pink and it is the only pink truly stable in glass melts. Other colours are obtained by mixing REE with other elements (Gupta and Krishnamurthy, 2005).

LED bulb. Ingrey publishing.

REE are important in glass due to their ability to absorb ultraviolet light. Cerium is used in glass bottles to protect the product and prevent browning of the glass due to radiation. Sunglasses contain cerium as well as neodymium and praseodymium to provide UV protection. Lanthanum is an integral part of camera lenses as low silica glass containing lanthanum oxide has a high refractive index[65] and low dispersion[66]. Optical lenses containing gadolinium are used for magneto-optical and electro-optical systems (Gupta and Krishnamurthy, 2005). Praseodymium is used for anti-reflection coatings on lenses and as a constituent of tinted glass filters for selective light absorption (Jackson and Christiansen, 1993).

Substantial amounts of cerium concentrates and oxide are used to polish glass surfaces. Cerium is especially suitable as a polishing agent as it removes glass by both chemical dissolution and mechanical abrasion making it more efficient than other agents such as silica and zirconia. The majority of polished glass products, for example mirrors, television faceplates and cathode ray tubes are finished using cerium oxide (Haxel et al., 2002).

Ceramics

REE oxides are essential in ceramics. Both the strength and toughness of structural ceramics is improved by adding REO (yttrium oxide and cerium oxide in particular) as stabilisers and sintering[67] aids to reduce sintering temperature and production costs. REO are also important in functional ceramics such as semiconductor sensors, microwave dielectric[68] and piezoelectric[69] ceramics (Guanming et al., 2007). Ceramic applications accounted for six per cent of global consumption of REE in 2008 and three per cent by value (Kingsnorth, 2009).

Rare earth oxides are used in ceramic capacitors[70] to alter the temperature-compensating, dielectric and permeability properties of the various barium titanite ceramic dielectrics. Adding lanthanum, cerium, praseodymium and neodymium results in a stable dielectric constant and gives the capacitor a longer life span (Roskill, 1986).

Small amounts of rare earth oxides are used as colourants in ceramics. For example, praseodymium added to zirconia and silica makes a yellow pigment, yttrium gives an orange colour and neodymium a light purple. These pigments are stable at high temperatures so can be used in single and double firing processes (Gupta and Krishnamurthy, 2005).

Refractories are materials that retain their strength at high temperatures and are commonly used to make crucibles.

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[65] Refractive index: a measure of how much the speed of a wave is reduced inside that medium compared to the speed of the wave in a reference medium.

[66] Dispersion: the phenomenon in which the phase velocity of a wave depends on its frequency.

[67] Sintering: a method for making objects from powder, by heating the material in a sintering furnace.

[68] Dielectric: non-conducting or insulating material.

[69] Piezoelectric: a substance that produces an electric charge when a mechanical stress is applied.

[70] Capacitor: an electric device consisting of two electrical conductors isolated from one other by a dielectric material, capable of storing electrical energy for release at some predetermined time.

Yttrium oxide, and to a lesser extent cerium oxide, are used in crucibles to protect the principal refractory material, usually zirconia (Roskill, 1986).

Other applications

REE have a range of applications in nuclear energy due to their ability to absorb neutrons and remain stable at high temperatures (Jackson and Christiansen, 1993). Gadolinium is used as a 'burnable poison', especially in boiling water reactors, to even out the performance of the reactor over time. Gadolinium oxide is a neutron absorber which decays under neutron exposure, compensating for the progressive build up of other absorbers as the uranium oxide fuel is used up (World Nuclear Association, 2009). Europium is used for control rods to regulate reactor operation as it is a good neutron absorber (Gupta and Krishnamurthy, 2005).

REE are widely used in pigments and paints. Cerium compounds are used to coat lead chrome paints to make them more resistant to fading due to light exposure. Cerous acetate is used to treat titanium dioxide pigments to make them more durable and resistant to sunlight (Gupta and Krishnamurthy, 2005). Yttrium is used as a coating to provide corrosion resistance and a lead-free surface primer for paints (Hedrick, 2001).
The rare-earth elements (REE) have a wide variety of defence applications. Examples of defence technologies dependent in REE are optics, surveillance and protection, sonar transducers[71], microwave communication, power and communications, guidance and control, lasers and aircraft materials (Molycorp, 2009).

There are many medical applications of REE, for example gadolinium provides better imaging of tumours. Also RE magnets are important for medical applications, such as Magnetic Resonance Imaging (MRI) equipment. Permanent magnets are being used to replace expensive traditional systems of super cooling wire coils in liquid helium systems to reduce the electrical resistance in the wire coils. This enables the MRI machines to be wider and less claustrophobic for the patient (Avalon Rare Metals, 2010).

REE have been used in agriculture as a fertiliser, mainly in China. REE solutions or compounds are added during production of calcium superphosphate to create a rare earth phosphate fertiliser (REPF) containing between 0.04 and 0.16 per cent REE. Research has shown that this REPF can improve crop yields, decrease diseased plant rates and increase quality (Xiangsheng et al., 2006).

New technologies

As research and technology continues to advance many more applications for REE are being developed and discovered, especially in the areas of energy conservation and efficiency and environmental protection.

There are several applications for REE in new electronic technologies, for example, sub-light-speed computer processors, advanced satellite communication systems and advanced superconductors[72]. As advances are made in materials science it is likely there will be further applications for REE, including in nano-particle technologies (Kennedy, 2010).

Magnetic refrigeration

Magnetic refrigeration is a new technology dependent on REE which is more environmentally friendly and efficient than standard refrigeration methods. Magnetic refrigeration is based on the magnetocaloric effect (MCE) which is the response of a magnetic solid to the application of a magnetic field. When the magnetic field is lowered the electrons[73] within the material spin in a higher energy state[74], absorbing heat from the material and causing the temperature to fall (Dieckmann et al., 2007). Gadolinium has been found to exhibit this effect strongly and has been suggested as the magnetic refrigerant. For the magnetic field source the most practical option in both household and transport applications is neodymium–iron–boron magnets (Gschneidner and Pecharsky, 2007).

Given the reliance of modern society on refrigeration, the advantages offered by magnetic refrigeration over conventional methods are considerable. It is also more environmentally friendly on account of its higher cooling efficiency. This higher energy efficiency results in less carbon dioxide being released. In addition no ozone-depleting or hazardous chemicals are involved (Brück et al., 2007). It has been calculated that REE magnets will make it possible to reduce up to 15 per cent of global fossil fuel consumption associated with cooling and refrigeration while eliminating harmful chemical compounds currently used (Kennedy, 2010). There are still a number of issues to be resolved before the first commercial units can

[71] Sonar transducer: a device used under water to convert electrical energy to sound energy and sound energy to electrical energy.
[72] Superconductor: a material through which electricity flows with zero resistance.
[73] Electron: a subatomic particle that carries a negative electric charge.
[74] Energy state: definite stable energy that a physical system can have; used especially of the state of electrons in atoms or molecules.

be released into the market. However, if commercialised, this technology could have a significant impact on REE demand (Gschneider and Pecharsky, 2007).

Fuel Cells

REE are essential in solid oxide fuel cells (SOFC). These are a clean, low-pollution technology to electrochemically generate electricity at high efficiencies. The SOFC is one of the most promising fuel cell technologies. However, conventional SOFCs face challenges in commercialisation due to the high cost of the performance. Recent research has shown that electrolytes[75] made using industrial grade mixed lanthanum, cerium and praseodymium (LCP) carbonates are able to achieve excellent fuel cell performance at low temperature making them more cost effective. SOFC's are a potentially important future use of REE (Zhu et al., 2008).

A considerable amount of work has been undertaken in recent years to develop fuel cells as power generators for zero emission electric vehicles. As noble metals such as platinum or palladium are used as a catalyst, the high cost of fuel cells has always been a limiting factor. Research has examined the use of the REE-based AB5-type hydrogen storage alloy[76] as a noble metal-free catalyst (Hu and Noréus, 2003). Although research to date is promising, currently no lower cost catalyst material has been found that will produce sufficient energy density[77] for transportation use (Frenette and Forthoffer, 2009).

Water Treatment

New technologies are being developed which will use REE in water treatment. Molycorp, together with the United States army, have invented a portable device to purify water by selective adsorption. They have also developed this technology for use in the mining and smelting industries to remove arsenic by converting it to a concentrated and extremely stable compound for easy filtering and disposal. It is suggested that the process would consume just a fraction of the volume of raw materials required by conventional sequestration methods and would produce only one-third of the waste volume (Molycorp, 2009).

World resources and production

Resources

An accurate figure for global rare earth resources is not known due to the quality and availability of data. USGS estimates total world reserves of rare earth oxides to be 99 million tonnes. China dominates world reserves with 37 per cent. China is followed by the Commonwealth of Independent States with 19 per cent, the United States with 13 per cent and Australia with 6 per cent. The remaining 22 per cent of reserves is divided between Canada, Malaysia, Brazil, India, Greenland, South Africa, Namibia, Mauritania, Burundi, Malawi, Vietnam, Thailand, and Indonesia (Table 4 and Figure 9; Hedrick, 2010).

China

China has the most abundant REE resources in the world, possessing hard rock, placer and ion adsorption clay deposits. The Bayan Obo bastnäsite deposit is the largest deposit in the world and contains reported reserves of at least 48 million tonnes at 6% REO (Kanazawa and Kamitani, 2006). A significant proportion of China's resources is contained in ion adsorption deposits. Importantly these deposits are rich in the less common HREE and these deposits are thought to contain about 80 per cent of the world's resources of HREE (Vulcan, 2008). China's additional reserves occur as placer deposits, largely in the coastal areas of west Guangdong and Hainan Island and associated with alkaline rocks, for example the Weishan deposit, in Shandong Province.

Commonwealth of Independent States

The REE resources of the CIS are dominated by loparite deposits (Kosynkin et al. 1993). Russia has significant REE resources in the apatite-nepheline ores of the Kola Peninsula but REE are not currently being extracted during the processing of these ores (Naumov, 2008). Total reserves of the CIS are estimated at 19 million tonnes (Hedrick, 2010). Kyrgyzstan has significant reserves of REE estimated at 51 500 tonnes (Bogdetsky et al., 2005). Kazakhstan has potentially significant REE resources associated with uranium mine tailings.

USA

The United States hosts the world's third largest reserves of REE at 13 million tonnes. The largest deposit is Mountain Pass in California which was exploited until 2002 and which Molycorp plans to bring it back into production by 2012 (Hedrick, 2009). The deposit is reported to contain 4.3 million tonnes of REO (Kingsnorth, 2008a). Another important resource in the US is at the Bear Lodge

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[75] Electrolyte: a solution that conducts electricity.

[76] AB5 alloys: commercial alloys usually of the type Mm(nickel, cobalt, aluminium, manganese)5, containing typically 10 wt% Co. Mm denotes Mischmetal, a cost-effective mixture of the rare earths La, Ce, Pr and Nd.

[77] Energy density: the amount of energy stored in a given system or region of space per unit volume, or per unit mass.

Country	Reserves (tonnes)
China	36 000 000
Commonwealth of Independent States	19 000 000
United States	13 000 000
Australia	5 400 000
India	3 100 000
Brazil	48 000
Malaysia	30 000
Other Countries	22 000 000
World Total	99 000 000

Table 4 Estimated world REE reserves (reserves are defined by USGS as that part of the reserve base which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials (Hedrick, 2010).

project in Wyoming which is currently being explored by Rare Element Resources Ltd. Exploration at the Bokan Mountain uranium project in Alaska indicates potentially significant concentrations of light and heavy rare earth elements associated with the uranium mineralisation (Ucore Uranium, 2010) A historic resource estimate produced by the USGS indicates 374 million lbs of REO at Bokan Mountain (Hiyate, 2010). Exploration by Great Western Metals Group on the Deep Sands heavy mineral sands deposit in Utah has revealed potentially extensive REE mineralisation. Surface sampling has returned grades in the range of 0.14–0.80% REO (Great Western Metals Group Ltd, 2010). REE resources are also present in Idaho, Montana and Missouri (Hedrick, 2008).

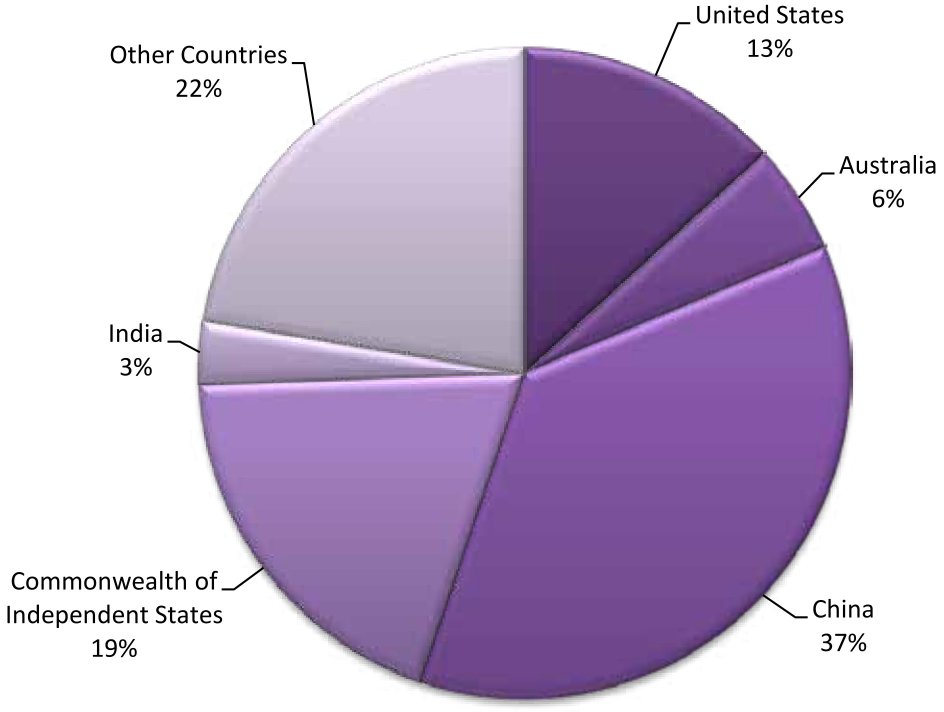
Australia

Australia has the fourth largest reserves of REE in the world, distributed across a range of deposit types. The Mount Weld deposit in Western Australia, notable for the high grade of the mineralisation, has a total resource of 12.24 million tonnes at a grade of 9.7% REO. The polymetallic Olympic Dam deposit in South Australia is estimated to contain 45 million tonnes of REO. However, the material is of too low grade (0.5% REO) to be currently exploited. Australian has significant REE reserves (3.4 million tonnes) in heavy mineral sands containing monazite, but these are not worked due to radioactivity issues (Lambert et al., 2008). Other Australian resources of note include the Dubbo Zirconia project (owned by Alkane Resources), Nolans Bore (owned Arafura Resources), Cummins Range (owned by Navigator Resources) and WIM 150 (owned by Australian Zircon).

Canada

Canada has substantial undeveloped REE resources. The Hoidas Lake project (owned by Great Western Minerals

Figure 9 Global distribution of REE reserves (Hedrick, 2010).



Rare earth element bearing sands, Deep Sands, Utah. © Great Western Minerals Group Ltd.

Group) is the most advanced, with reserves of 2.6 million tonnes at 2.43% REO (Billingsley, 2010). A further significant resource occurs at Thor Lake (owned by Avalon Rare Metals). The deposit contains total Inferred Mineral Resources of 64.2 million tonnes at 1.96% REO (Avalon Rare Metals, 2009). A number of other, relatively early stage projects are being evaluated in Canada.

Greenland

It has been suggested that Greenland contains REE resources which could potentially meet about 25 per cent of global demand (Lewis, 2009a). The Kvanefjeld deposit in the Ilimaussaq intrusion is estimated to contain of 4.91 million tonnes REO. Greenland Minerals and Energy have completed an interim report from the feasibility study suggesting that the mine will have an annual output of more than 43 000 tonnes REO (Batten, 2010).

Africa

South Africa has what is claimed to be the highest grade REE deposit in the world, the Steenkampskraal monazite deposit, with an average grade of 17% REO and a reserve of 29 400 tonnes REO (historic figures, GWMG Ltd, 2009). A further notable resource in South Africa is Frontier Minerals' Zandkopsdrift carbonatite deposit. The Kangankunde deposit (owned by Lynas Corp) in Malawi is estimated to contain an inferred resource of 107 000 tonnes REO (Lynas Corp, 2007). Also in Malawi the Machinga REE project, rich in HREE, has recently been acquired by Globe Metals and Mining but is still in the very early exploration stages (Globe Metals and Mining, 2009). The Tantalus project in Madagascar is estimated to contain 14.4 million tonnes of material grading 1.52% REO (Industrial Minerals, 2009a). A monazite-rich laterite, overlying a carbonatite at Mrima Hill in Kenya is reported to contain six million tonnes of material with about five per cent REO. A major carbonatite- associated deposit occurs at Etaneno in Namibia and is estimated to contain 20 million tonnes of REO. Other resources in Africa include: the Karonge hard rock bastnäsite deposits in Burundi; the hard rock monazite Bou Naga deposit in Mauritania; the Congolone heavy mineral sands in Mozambique; and the Nile Delta and Rosetta placer monazite in Egypt (Gupta and Krishnamurthy, 2005).

South and east Asia

India contains both hard rock and placer deposits and the USGS estimates that the country has 3.1 million tonnes of reserves (Hedrick, 2010). Official figures reported by the Department of Atomic Energy indicate that in 2005 India had 10.21 million tonnes of monazite in beach and inland placer deposits (Indian Minerals Yearbook, 2008).

Vietnam is known to have rare earth deposits, for example in the Dong Pao area. However, reliable resource data is currently unavailable. Heavy mineral sand REE reserves area also present in Thailand, Indonesia and Malaysia (Gupta and Krishnamurthy, 2005).

South America

Brazilian REE reserves are estimated at 48 000 tonnes (Hedrick, 2010). These reserves include placer and hard rock deposits (Jackson and Christiansen, 1993). The Araxá carbonatite complex is reported to contain 800 000 tonnes of laterite averaging 13.5% REO (Castor and Hedrick, 2006). Important REE resources also occur in Argentina and Uruguay.

Production

Historical production

REE were initially produced in minor quantities from granite pegmatites, the first geological environment in which they were identified (Castor and Hedrick, 2006). India and Brazil were the world's main sources of REE from these deposits until the 1940s when Australia and Malaysia began production primarily of monazite from placer deposits. Between the 1960s and 1980s bastnäsite carbonatite deposits started to be exploited and the United States was the principal producer (largely from Mountain Pass) followed by Australia (Naumov, 2008). During the 1980s China began to produce REE, mainly from the Bayan Obo deposit, overtaking the United States to become the world's largest producer by 1988 (Gupta and Krishnamurthy, 2005).

China now dominates world production of REE, accounting for 96.8 per cent of supply (Chinese rare earth industry report, 2009). Producers in other countries were generally unable to compete with low priced Chinese exports. The exception was the Mountain Pass mine in California which remained active until 2002 when environmental issues resulted in its closure. REE prices at this time were relatively low and no new deposits have since been developed, resulting in the current situation of virtually no REE mines outside China.

Current production

The only countries known to be actively mining REE are China, India, Brazil and Malaysia. Since the closure of Mountain Pass mine in 2002, the USA has not been mining REE ore but has been producing REE products using stockpiled material, although this production is not disclosed in official figures (Hedrick, 2009). In addition REE minerals are believed to be produced in Indonesia, Kazakhstan, Democratic P.R of Korea, Republic of Korea, Kyrgyzstan, Mozambique, Nigeria, Russia and Vietnam but reliable estimates of quantities are difficult to obtain. Total reported world production of REO in 2008 was 126 000 tonnes, a four per cent increase compared to 2007 (121 000 tonnes). World production has more than doubled in the last 15 years (Figure 10). Peak production was in 2006 with over 134 000 tonnes.

Chinese production of REE has been increasing and 125 000 tonnes of REO were produced in 2008, accounting for in excess of 95 per cent of global production (Figure 11). Production is primarily from Bayan Obo (46 000 tonnes REO annually) as a by-product of iron ore mining, but also from bastnäsite-bearing carbonatites in Sichuan and Mianning (31 000 tonnes REO annually) and ion adsorption clays in Southern China (7000 tonnes REO annually) (London, 2009). The major producers of REE in China are the Batou Iron and Steel Group, Batou Rare Earth Group, Gansu Rare Earth Corp and Sichuan Rare Earth Group (Naumov, 2008).

India is thought to be producing REE from beach sands placer deposits. Although recent production data is unavailable in 2006 and 2007 45 and 35 tonnes of rare earths were produced respectively, mainly rare earth fluorides, cerium oxide and cerium hydrate from conversion of rare earths chloride (Indian Bureau of Mines, 2008). Rare earth companies include Indian Rare Earth Ltd which produces yttrium oxide and Kerala Minerals and Metals Ltd which extracts monazite from heavy mineral sands (Naumov, 2008).

Brazil produces REE from monazite and production has been gradually increasing since 2004. There are also plans to produce REE as a by-product from the Taboca Pitinga tin mine in a joint venture between Canada's Neo Material Technologies Inc. (NMT) and Japan's Mitsubishi Corp (Industrial Minerals, 2009b).

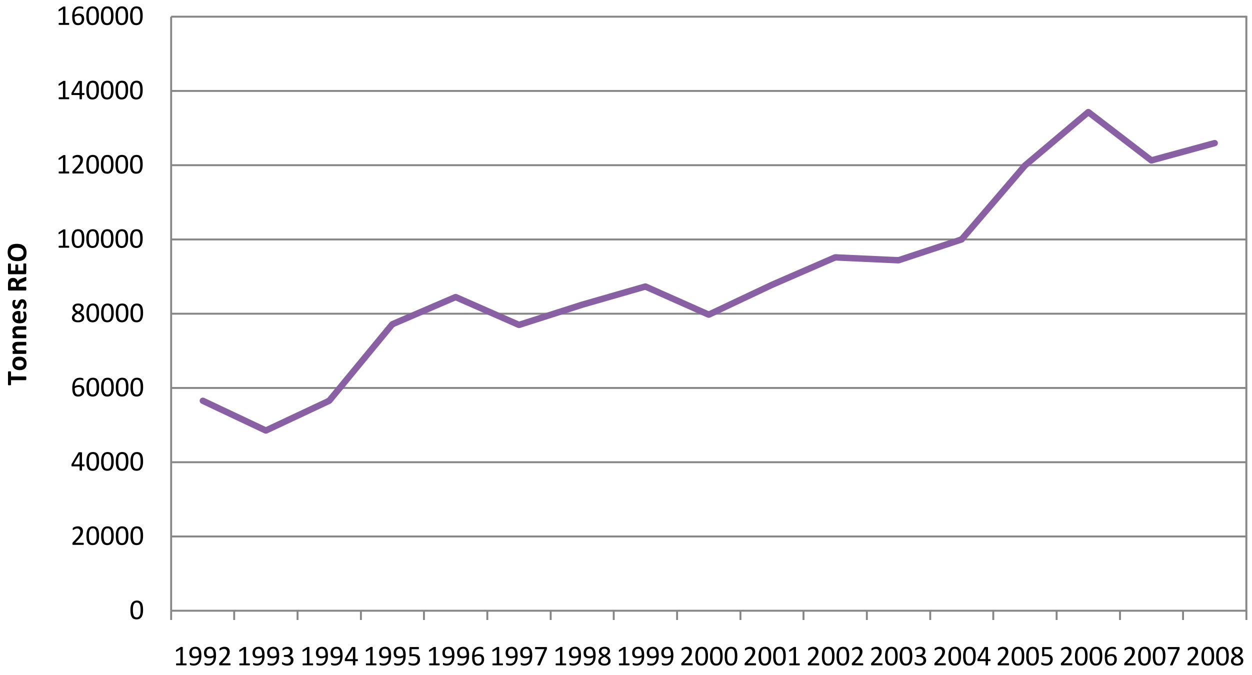


Figure 10 Annual reported world production of REO between 1992–2008 (World Minerals Statistics Database, BGS).

Malaysia currently produces monazite as a by-product of tin extraction and has produced xenotime in the past. Production fluctuates each year and in 2008 was only 233 tonnes of monazite. Lynas Corp, the company developing the Mount Weld deposit in Australia, has decided to build its processing plant in Malaysia, with plans to produce 11 000 REO tonnes per year by 2011 (Curtis, 2009).

Although ore is not currently being mined at Mountain Pass the separation plant at the site has been in operation since 2007 using stockpiled material to produce bastnäsite concentrates, and REE intermediates and refined products (Hedrick, 2009).

Production data is not available for the CIS. In the 1990s Russia was one of the world's largest producers of REE but since 2001 virtually none has been produced (Polyakov, 2001). Kyrgyzstan was a significant producer of REE in the 1980s providing a significant proportion of the former USSR's REE in addition to exporting to Japan, South Korea and Germany. The REE mines are no longer operational although the country is still producing REE from inventories (Bogdetsky et al., 2005).

Projects under development

China's dominance of the global REE industry has resulted in concerns over security of supply. This, in conjunction with the growing demand for REE, particularly for 'green' technologies, has resulted in considerable exploration interest in recent years. Over 100 deposits in Australia, Canada, South Africa and the USA are being investigated for their REE potential and several have reached the resource evaluation and metallurgical testing stages (O'Driscoll, 2010; Table 5).

Molycorp Minerals bought the Mountain Pass operation in 2008, planning to reopen the mine and rejuvenate REE processing. RE oxides, alloys (NdFeB) and metals will be produced rather than just oxides, as had been previously produced from the mine. Production of 3000 tonnes of REO is forecast for 2010–2011, increasing to 20 000 tonnes by 2012 (O'Driscoll, 2010).

Lynas Corporation Ltd. began mining the Mount Weld bastnäsite deposit in 2007 and has stockpiled about 773 000 tonnes of ore (Curtis, 2009b). A concentration plant is under construction in Malaysia and there is currently no recorded production of REO from Australia (Miezitis, 2009). Production is expected to start in 2011 at an annual rate of 11 000 tonnes which will later increase to about 22 000 tonnes. This would be equivalent to about 14 per cent of the current global REO market (Hampton, 2009).

Stans Energy Corp, has recently acquired an exploration licence for the REE-bearing Aktyuz Ore Field in Kyrgyzstan, as well as the Kutessay II mine, once the Soviet Union's primary source of REE (Industrial Minerals, 2010a).

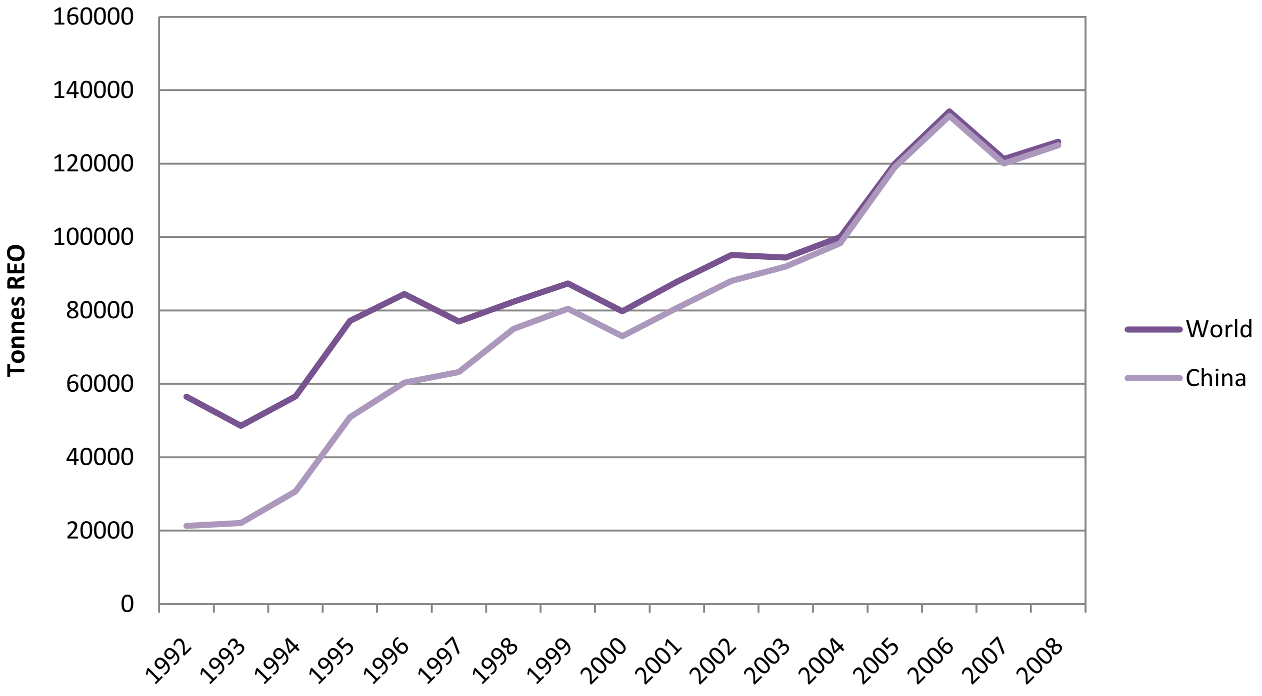


Figure 11 Chinese and world production of REO between 1992–2008 (World Minerals Statistics Database, BGS).

Deposit	Company	REO reserves (million tonnes)	Ore reserves (million tonnes)	Grade (% REO)	Project status
Mountain Pass, USA	Molycorp Minerals	4.3	50	8-9 (5% cut-off)	Feasibility study, production anticipated for 2010-2011
Mount Weld, Australia	Lynas Corporation Ltd.	1.18	12.24	9.7 (2.5% cut-off)	Construction. Mining began in 2007, production anticipated for 2011
Nolans Bore, Australia	Arafura Resources Ltd.	0.85	30.3	2.8 (1% cut-off)	Feasibility study, production anticipated for 2012
Dubbo Zirconia, Australia	Alkane Resources Ltd		35.7	0.745% REO, 0.14% Y_2O_3	Feasibility study, production anticipated for late 2011
Kvanefjeld, Greenland	Greenland Minerals and Energy Ltd.	4.91	457	1.07	Pre-feasibility. Construction to begin 2013, production by 2015
Hoidas Lake, Canada	Great Western Minerals Group Ltd.	0.07	2.6	2.43 (1.5% cut-off)	Pre-feasibility
Bull Hill Southwest (Bear Lodge), USA	Rare Element Resources Ltd.		9.8	4.1 (1.5% cut-off)	Advanced exploration
Kangankunde Hill, Malawi	Lynas Corporation Ltd.	0.12	2.53	4.24 (3.5% cut-off)	Advanced exploration
Nechalacho (Thor Lake – Lake Zone), Canada	Avalon Rare Metals Inc.		64.2	1.96	Pre-feasibility
Cummins Range, Australia	Navigator Resources Ltd.	0.07	4.17	1.72 (1% cut-off)	Advanced exploration
Steenkampskraal, South Africa	Rare Earth Extraction Co. Ltd. & Great Western Minerals Group Ltd.	0.03*	0.25*	17*	Closed, due diligence
Strange Lake, Canada	Quest Uranium		52*	1.3 REO, 0.66 Y_2O_3*	Advanced exploration
Kutessay II, Kyrgyzstan	Stans Energy Corp.	0.06*		0.41*	Advanced exploration
Eco Ridge, Canada	Pele Mountain Resources	Predominantly a uranium project but significant concentrations of REO have been identified			Feasibility study
Archie Lake, Canada	Quantum Rare Earth Development Corp.	Early exploration stage, recent chip sampling has returned an average grade of 3.8% REE+Y			
Deep Sands, USA	Great Western Minerals Group Ltd.	Early exploration stage, surface sampling has returned grades in the range of 0.14% to 0.8% REO			
Lofdal, Namibia	Etruscan Resources Inc.	Early exploration stage, surface sampling has returned an average grade of 0.7% REE+Y			
Yangibana, Australia	Artemis Resources	Early exploration stage, rock chip sampling has returned an average grade of 2.84% REO			
Machinga, Malawi	Globe Metals and Mining	Early exploration stage, rock chip sampling has returned a maximum value of 2.64% REO			

*Table 5 The size and status of selected REE projects. *Historical data.*

Kazakhstan does not currently have any operating REE mines. However, an arrangement has been made between Sumitomo Corp and Kazatomprom to produce REE from uranium ore residue. This source is expected to produce about 3000 tonnes of REE a year, supplying about 10 per cent of Japan's current demand (Lewis, 2009b).

Despite there being plentiful REE resources elsewhere in the world it is possible that alternative sources may struggle to compete with China. Not only is mine development an expensive and time consuming process, it has been suggested that with the current monopoly China could easily control REE pricing to the detriment of competitors (Kennedy, 2010). Furthermore Chinese production is likely to remain more competitive as a significant proportion is derived as by-product of iron mining and the ion adsorption clay deposits are relatively cheap and easy to process (Cox, 2009).

World trade

The current value of the REE market is about US$1.25 billion (2008), relatively small compared with many other minerals. The REE market is more complicated than many others because of the large number of elements and their broad range of applications for which demand fluctuates over time, largely as a result of technological developments. The market has a history of abrupt and dramatic changes. Demand for the individual REE has fluctuated markedly in recent decades. For example when the colour television was introduced demand for europium increased sharply. However, by the 1960s samarium was the dominant REE being used by industry for the production of samarium-cobalt magnets. In the 1980s neodymium magnets became widely used resulting in considerable demand for this element. Recent technological innovations have led to increased demand for dysprosium and terbium (Cox, 2009).

Historically the balance of demand and supply in the world rare earth market has been fairly stable. However, in the last three years the market has changed substantially from a position of oversupply to demand shortages (Roskill, 2007). Total REO demand in 2008 was 124 000 tonnes, an increase of 45 per cent compared to 2003 when demand was only 85 000 tonnes (Avalon Rare Metals Inc., 2009). Total demand is predicted to reach 170 000 to 190 000 tonnes by 2014 (O'Driscoll, 2009).

Significant growth is forecast in most sectors of REE consumption, particularly for magnets and metal alloys which have predicted annual growth rates of 10–15 per cent and 15–20 per cent respectively (Table 6; Kingsnorth, 2009).

Supply constraints have recently led to considerable reliance on illegal supply from China. Statistics indicate that about a third of the 39 000 tonnes of REE exported from China in 2008 was smuggled (O'Driscoll, 2009). Illicit exports are typically in the form of REE mixed with steel, exported as steel composites, making them hard to detect. The process is reversed in the importing country, recovering the REE (Bradsher, 2009). An official at the Ministry of Economy, Trade and Industry suggested that Japanese industry, the world's largest importer of REE, has become reliant on illicitly imported metals (Lewis, 2009b).

Imports and exports

Imports of REE compounds and metals are dominated by Japan, USA, Germany, Austria and France. The largest importer of REE compounds in 2008 was Japan at just over 28 000 tonnes. 2008 data is not available for the USA but in 2007 nearly 24 000 tonnes of imports were reported. These two countries were followed by Germany importing 11 000 tonnes, France (10 000 tonnes) and Austria (7000 tonnes; Figure 12). Japan is also by far the largest importer of REE metals at 6300 tonnes. Japan is followed by China Hong Kong

Mt Weld open pit. © Clint Cox, The Anchor House, Inc. 2010.

SAR[78] with 1000 tonnes, USA, Austria, Brazil and France, all importing about 500 tonnes of metal (UN comtrade, 2010).

China exported 48 000 tonnes of REE compounds in 2008, greater than four times as much as the next largest exporter, Austria, which is not a primary producer of REE. The Austrian-based company Treibacher AG exports a diverse range of REE products, including oxides of all the REE, ferrocerium/lighter flint alloys, hydrogen storage alloys, individual REE metals, mischmetal and fifteen cerium compounds and solutions (Hedrick, 2002). Austria exported just over 11 000 tonnes of REE compounds in 2008. The third largest exporter was Japan at 9000 tonnes, followed by Russia with 6000 tonnes. Other significant exporters of REE compounds in 2008 were the USA, Estonia, France, Sri Lanka, Kazakhstan and the United Kingdom (Figure 13). China was also the largest exporter of REE metals, with a total of nearly 7000 tonnes. It was followed by the USA (1200 tonnes), Austria (370 tonnes) and Belgium (303 tonnes). The other countries shown in Figure 13 all exported less than 300 tonnes (UN comtrade, 2010).

Application	**Consumption REO (tonnes)**		**Annual growth rate %**
	2008	**2014 (forecast)**	
Catalysts	23 000	28–30 000	6–8
Glass	12 500	12-13 000	Negligible
Polishing	15 000	19–21 000	6–8
Metal alloys	22 500	43–47 000	15–20
Magnets	26 500	39–43 000	10–15
Phosphors and pigments	9000	11–13 000	7–10
Ceramics	7000	8–10 000	7–9
Other	8500	10–12 000	7–9
Total/range	124 000	170–190 000	8–11

Table 6 Global demand for REE in 2008 and 2014 (Kingsnorth, 2009).

Although China's REE production has been increasing in recent years it has been reducing export quotas for REO due to increasing domestic demand. China has also been increasing the tariffs on rare earth metals and oxides. In 2007 a 10 per cent export tariff was imposed, which was increased to 16 per cent in 2008. Closure of REE operations due to environmental concerns has further impacted on Chinese supplies. It has been suggested that restrictions to Chinese exports could force consumers to move manufacturing enterprises to China resulting in, higher value finished goods containing REE being exported rather than the REO (Hong, 2006). Accordingly there is growing concern about the security of future supplies of REE and many additional sources outside China are being evaluated as discussed above.

Industry commentators suggest there are sufficient reserves elsewhere in the world to not only compensate for reduction in China's REE supplies, but to ultimately supply any domestic Chinese shortfall (Lifton, 2009a). This view is supported by the USGS which indicates that undiscovered resources are thought to be very large relative to expected demand (Hedrick, 2010). In reality the supply-demand balance is likely to vary considerably for individual elements and between the light and heavy REE (Table 7). It appears that supply of the LREE will remain sufficient to meet global demand. However, there is greater concern over the supply of the HREE, the main source of which are ion adsorption clay deposits of southern China. As a result of the inefficient mining of these resources, there has been a significant reduction in recovery levels from these deposits (Industrial Minerals, 2009c). Predicted demand for individual REE varies but it has been estimated that demand will outpace supply for terbium, dysprosium and europium by 2014. The only LREE predicted not to meet demand is neodymium. Lanthanum, cerium and praseodymium are all predicted to be in surplus by 2014 (Table 7; IMCOA, 2009).

Prices

As with many minor metals, there are no exchanges on which REE metals are traded. Both the metals and their oxides are sold by specialist REE-trading companies (Vulcan, 2008). REO are typically supplied on long term confidential contracts and prices are set by producers.

There is currently significant variation in the price of different REE metals and oxides (Table 8 and Figure 14). Cerium oxide trades at about US$5 per kilogram whereas europium oxide is sold for US$525 per kilogram. HREE are

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[78] SAR: Special Administrative Region, a provincial-level administrative division in the People's Republic of China.

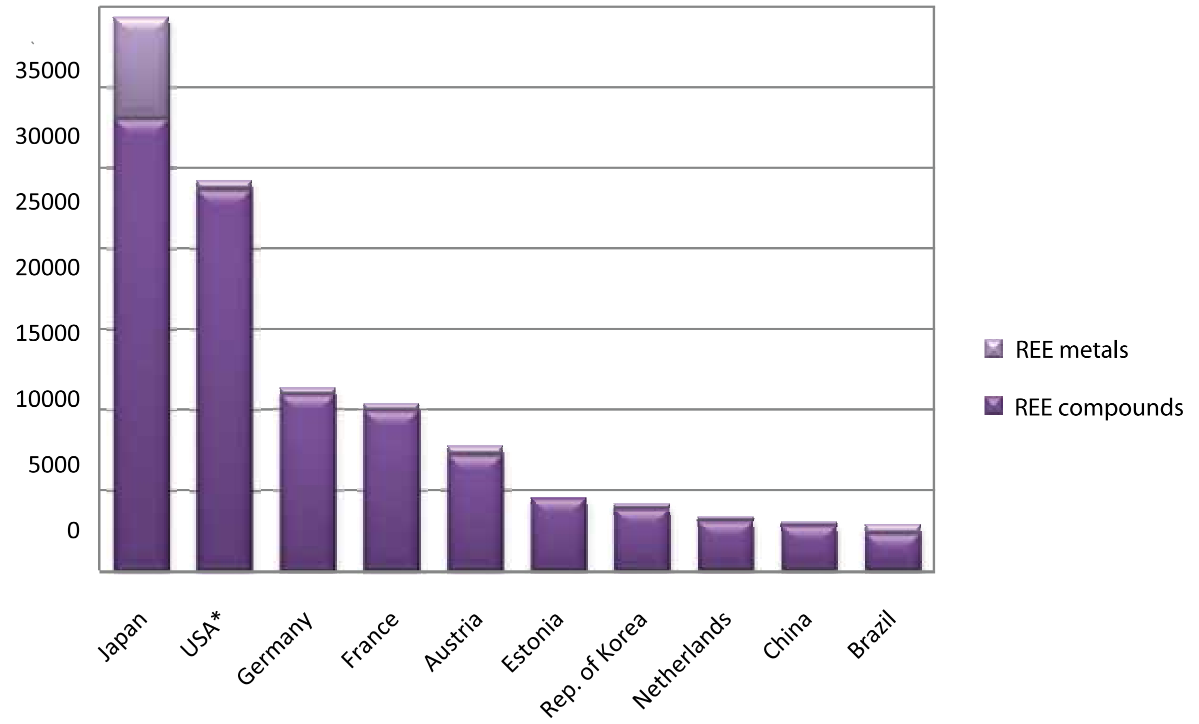

Figure 12 Major importers of REE compounds and metals in 2008. Source United Nations Commodity Trade Statistics Database (UN Comtrade) Nations with * indicates 2007 figures.

	Demand		**Supply**		
	REO tonnes	%	REO tonnes	%	Surplus/ deficit
Lanthanum	51050	28.4	54092	26.5	3042
Cerium	65750	36.5	79156	38.9	13406
Praseodymium	7950	4.4	9909	4.9	1959
Neodymium	**34900**	**19.4**	**33665**	**16.5**	**-1235**
Samarium	1390	0.8	4596	2.3	3206
Europium	**815**	**0.5**	**659**	**0.3**	**-156**
Gadolinium	2300	1.3	3575	1.8	1275
Terbium	**565**	**0.3**	**512**	**0.2**	**-53**
Dysprosium	**2040**	**1.1**	**1830**	**0.9**	**-210**
Erbium	940	0.5	1181	0.6	241
Yttrium	12100	6.7	12735	6.3	635
Ho, Tm, Yb, Lu	200	0.1	1592	0.8	1392
Total	180000	100	203502	100	

Table 7 Forecast supply/demand by element in 2014 (±15%) Those shown in bold are predicted to be in deficit by 2014 (IMCOA, 2009).

typically more expensive than lighter LREE due to their lower abundance in most deposits. The relative difficulty and associated expense in extracting each element is another factor which influences the price. The price of individual elements is also affected by demand patterns which vary with time. Furthermore REE prices are affected by the purity level of the product which is dictated by specific end-user requirements. Higher purities and other value-added properties attract higher prices (Lynas, 2009).

REE prices have fluctuated significantly since the 1950s, largely as a result of the supply/demand balance, related to environmental legislation and economic factors such as inflation and energy costs (Hedrick 1997).

Between 1958 and 1971 prices decreased largely as a result of the opening of the Mountain Pass Mine in California and widespread use of REE compounds and metals in commercial applications. Supplies continued to increase in the 1970s and demand kept pace. By the late 1970s operating costs had increased due to inflation and rising energy costs leading to an increase in prices. Prices were stable during the early 1980s. However, by 1985 a change in the petroleum industry to fluid cracking catalysts (due to environmental legislation) which use less REE resulted in decreased

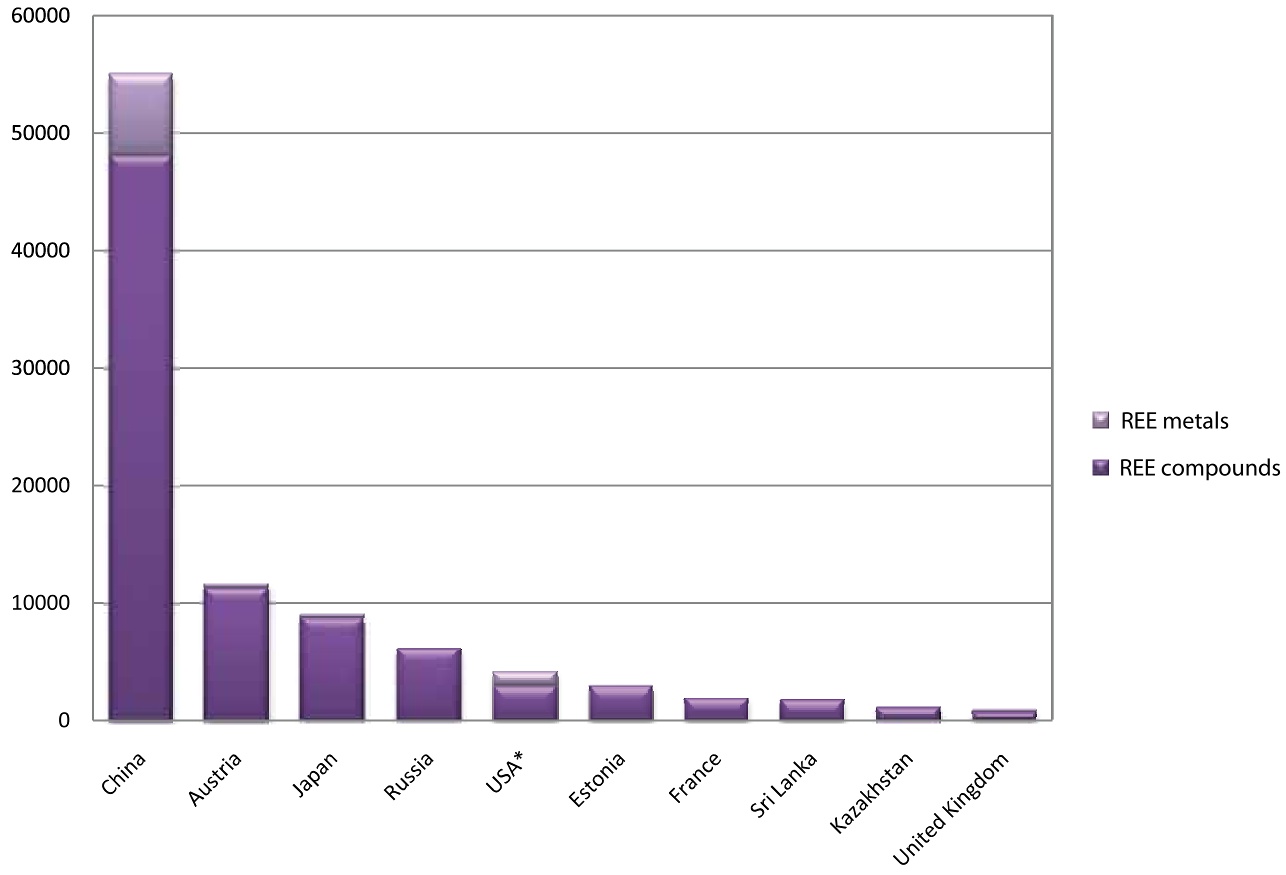

*Figure 13 Major exporters of REE compounds and metals in 2008. Source United Nations Commodity Trade Statistics Database (UN Comtrade) Nations with * indicates 2007 figures.*

REE	**Price ($ per kg)**	
	Metal	**Oxide**
Cerium	8.50–9	4.7–5.2
Dysprosium	240–260	188–198
Europium	770–800	515-535
Gadolinium	18.5–19.5	7.4–7.9
Lanthanum	10.5–11	6.2–6.5
Neodymium	41–43	30.5–31
Praseodymium	41–42	30–30.5
Samarium	20.5–21	4.25–4.75
Terbium	610–650	560–600
Yttrium	35–45	10.5–11.5

Table 8 REO and metal prices in April 2010. Prices shown are for a minimum 99% purity and are quoted in US$ per kilogram on an FOB China basis (metal -pages, 2010).

demand. Mine production decreased in response, leading to a rises in prices the following year (Hedrick 1997).

REE prices have been artificially low since the 1990s as a result of the Chinese REE industry growing so rapidly that supply exceeded demand. By 1995 demand for REE had increased considerably, causing concern over supply and placing upward pressure on prices. China reacted by increasing production, causing prices to reduce the following year (Naumov, 2008).

By 2000 demand for neodymium and dysprosium had increased dramatically due to their use in Nd-Fe-B magnets and China responded by increasing production of both metals and oxides. Because REE cannot be selectively mined this led to over production of other REE and a decrease in prices. In an attempt to combat this and help prices recover China decreased production. However, this failed due to a decrease in demand for telecommunication equipment and computers during the first half of 2001 resulting in supplies continuing to exceed demand (Naumov, 2008).

REO (purity 99% min)	Price ($ per kg)							
	La	Ce	Nd	Pr	Sm	Dy	Eu	Tb
2001	7	4	11	6.2	9	35	310	135
2002	2.3	2.3	4.4	3.9	3	20	240	170
2003	1.5	1.7	4.4	4.2	2.7	14.6	235.4	170
2004	1.6	1.6	5.8	8	2.7	30.3	310.5	398
2005	1.5	1.4	6.1	7.6	2.6	36.4	286.2	300
2006	2.2	1.7	11.1	10.7	2.4	70.4	240	434
2007	2.8	2.6	31.2	30.4	3.1	88.3	311	575
2008	8.8	4.4	32.9	32.6	4.8	120.8	491	740
2009	5.9	3.8	14.5	14.5	4.8	112	495	360
April 2010	6.4	5.0	30.8	30.3	4.5	193	525	580
%increase 2002–2008	284	95	656	728	61	504	105	335
%increase 2008–2009	-33	-13	-56	-56	-1	-7	1	-51

Table 9 REO price trends 2002–2010 (Lynas Corp, 2009; metal-pages, 2010).

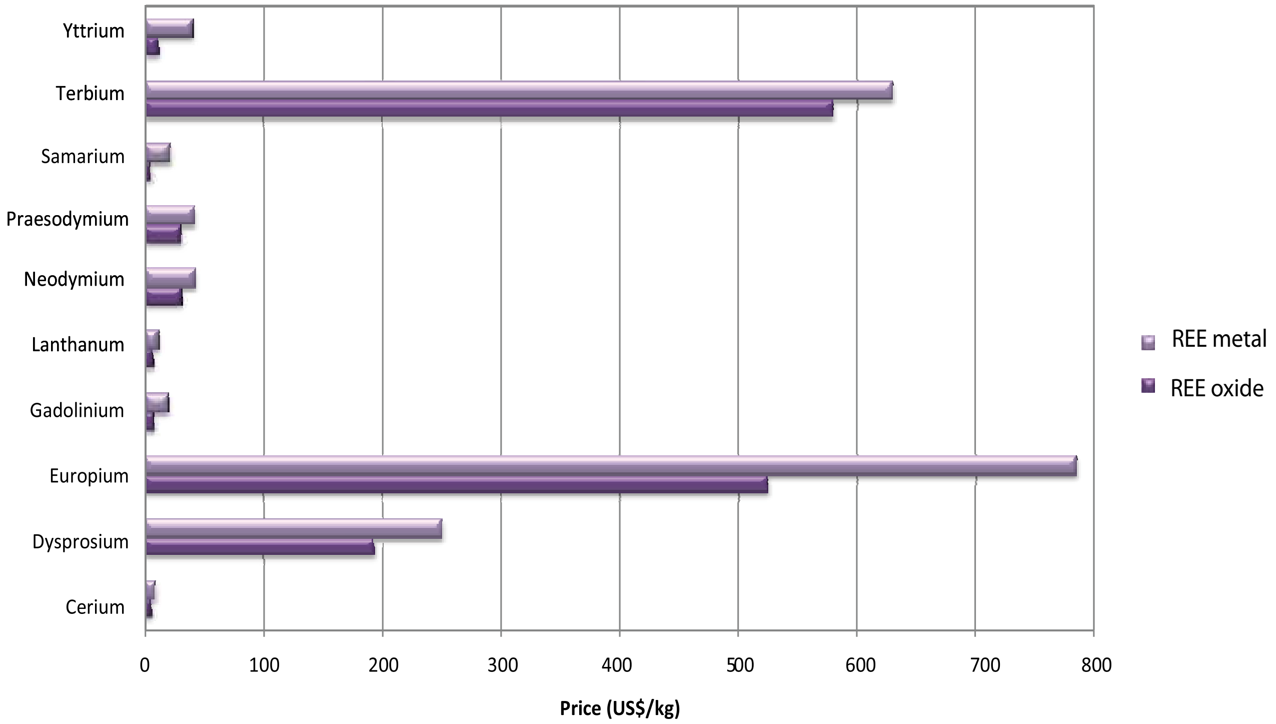

Figure 14 REO and metal prices in April 2010 (metal-pages, 2010).

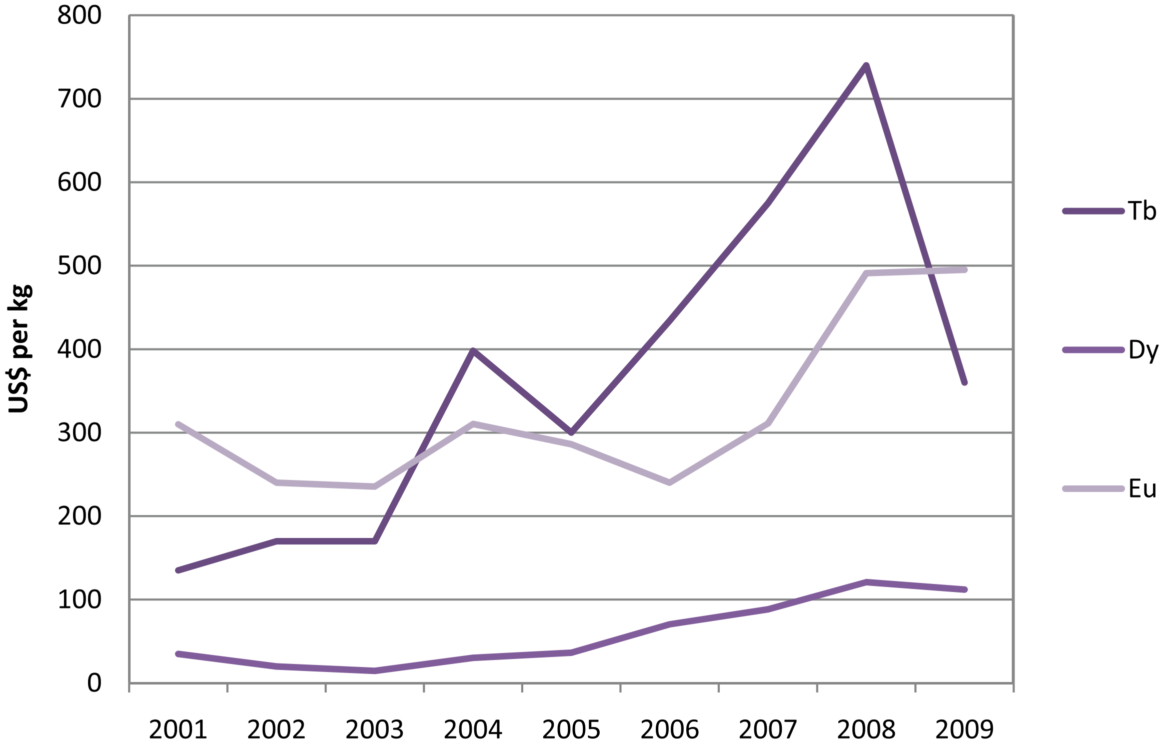

Figure 15 Price trends for selected HREO from 2001 to 2009 (Lynas Corp, 2010).

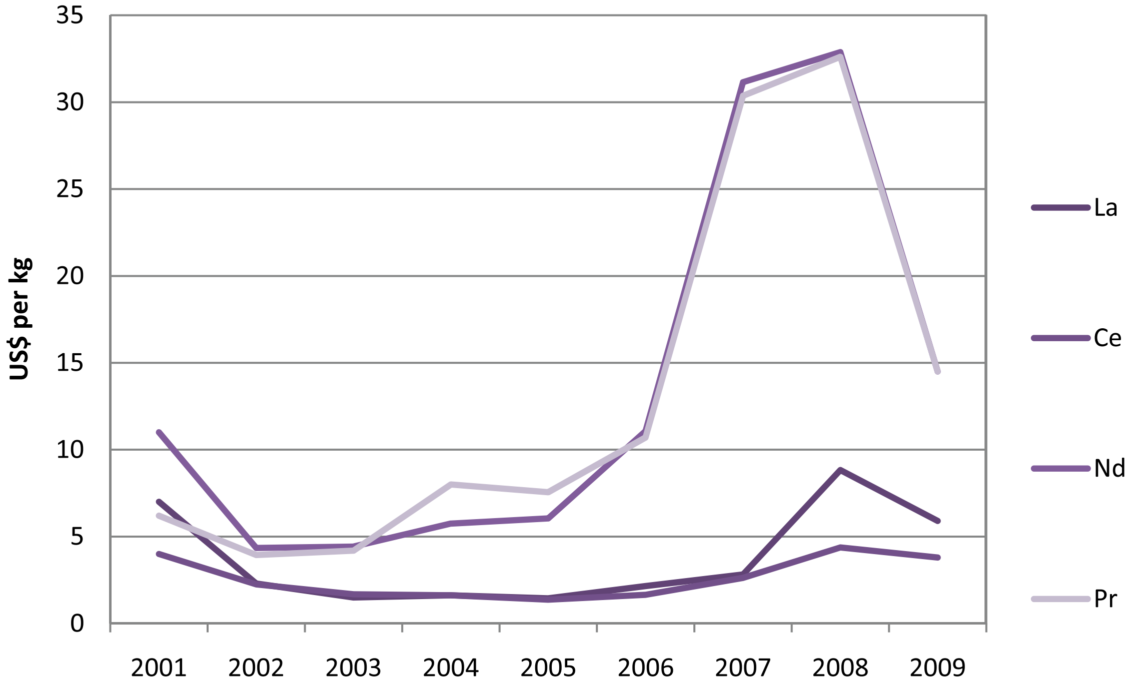

Figure 16 Price trends for selected LREO from 2001 to 2009 (Lynas Corp, 2010).

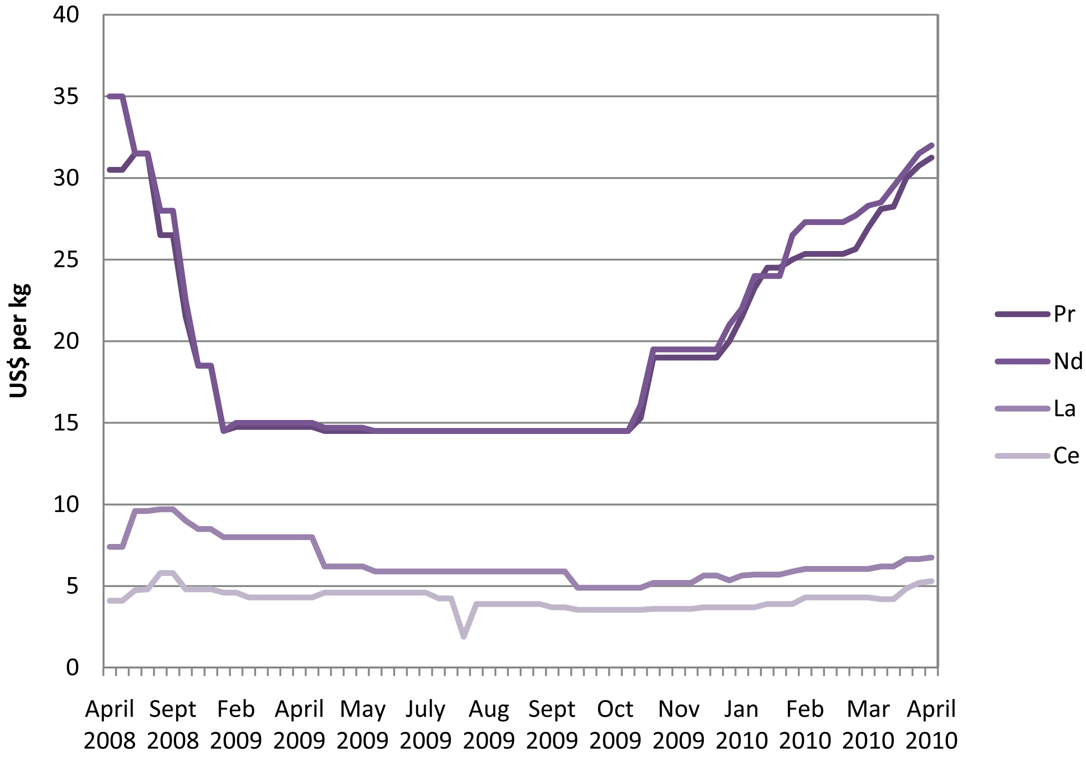

Figure 17 Price trends for selected REO from January 2008 to April 2010 (Industrial Minerals, 2010b).

Prices for most REO reached a low between 2002 and 2003 before gradually increasing until 2006 (Table 9). The rate of increase subsequently accelerated, peaking in the first half of 2008. Of the LREE oxides praseodymium and neodymium showed the largest rises, both increasing in price by approximately 700 per cent between 2002 and 2008. In addition to being rarer, the HREE became increasingly important in industry during the 2000s with the prices of dysprosium oxide and terbium oxide increasing by 500 and 300 per cent respectively between 2002 and 2008.

As with many resource-based sectors the REE industry has been deeply affected by the recession (Industrial Minerals, 2009d). During the second half of 2008 many industries began to use existing inventories to lower costs. This caused REE prices to decrease significantly; for example terbium fell to US$360 per kilogram, a decrease of more than 50 per cent from its peak of US$740 per kilogram in 2008 (Figure 15). Praseodymium and neodymium prices also both fell dramatically in the second half of 2008 before stabilising at that level for most of 2009 (Figure 16).

REE prices have been recovering since the final quarter of 2009 as demand has increased and supplies tightened (Figure 17). Prices for praseodymium and neodymium began to increase rapidly in October 2009 and had risen from US$14.5 per kilogram to US$30 and US$30.5 per kilogram respectively. By April 2010 these increases are due to escalating demand from key markets such as magnetic applications. Prices for cerium and lanthanum oxide have also started to rise, but not at the same rate as for praseodymium and neodymium. Lanthanum oxide prices are rising partly due to an improvement in the market for high purity glass for digital camera lenses (Russell, 2010). Dysprosium prices have been rising since the end of 2009 and reached a high of US$188-198 per kilogram in April 2010. The price for bastnäsite concentrate has stayed constant at US$2.25 per pound for at least the last 2 years.

Recycling and substitution

In recent years the REE market has been in over-supply and as a result there has been little incentive to investigate recycling technologies and substitutes. However, with rising prices and concerns about security of supply, secondary sources and recycling could reduce pressure on primary production.

Substitutes

Many of the applications of REE are highly specific and substitutes are either unknown or provide inferior performance (Haxel et al., 2002). Where substitutes exist they are commonly another REE or a more expensive material such as platinum-group elements. These for example can be used in petroleum cracking and autocatalysts in place of REE (Bonel and Chapman, 2005).

For approximately 20 years scientists have been trying to find alternatives for the neodymium-iron-boron magnet with no success (Smith, 2009b). Europium, used in the colour-cathode ray tube and LCD[79] in computer monitors, has a relatively low abundance, high demand and no substitute.

Substitution of REE by materials other than rare earths may be possible where metallurgical and magnetic properties are involved. However, in those applications based on specific optical, chemical and certain special magnetic properties substitution is less likely (Table 10). Consequently, for the foreseeable future it is assumed that REE will be required in polishing applications, catalysts, phosphors, magnets and optical glass components, colouring and decolouring glass, pigments and as intensifiers of x-rays (Gupta and Krishnamurthy, 2005).

Recycling

Only small quantities of REE-bearing scrap are recycled. REE are commonly used in compound form making recycling difficult and expensive. Manufacture of neodymium-iron-boron magnets increases annually and generates a significant amount of scrap so an effective means of recycling Nd from this source would be highly beneficial. However recycling neodymium from scrap is very difficult as it forms extremely stable compounds with several elements (Takeda et al., 2006). Several processes have been proposed for recycling REE magnets but they have not been developed commercially as magnets made from recycled materials do not have the same performance as those prepared from primary raw materials. This quality issue results from contamination by impurities, largely carbon and oxygen in recycled magnets (Itakura et al., 2006). Studies have also been undertaken to investigate recovering REE from optical lenses and polishing sludges. Neodymium was successfully removed from neodymium containing boron trioxide but further research is needed to improve the recovery rate by optimising the processing conditions (Saito et al., 2006).

Although recycling of magnets is problematic, reusing magnets is another option. In many applications the lifetime of the magnet is longer than that of the device in which it is used. For example, discs drives only last a few years and are generally disposed of containing functional magnets (Trout, 2007).

Application	REE Material	Alternative
Metallurgy		
Nodular iron	Misch metal	Magnesium
Steel	REE silicide	Calcium
Nuclear energy		
Control rod	Europium	Hafnium
Hydrogen storage		
	Lanthanum	Iron titanium alloy
	nickel alloy	
Glass		
Polishing	Cerium oxide	Plate glass (Pilkington) process
Ceramics		
Glazed ceramic tiles	Cerium	Tin, zirconium

Table 10 Alternatives to REE in some applications. (Gupta and Krishnamurthy, 2005).

Some manufacturers have established closed loop recycling programmes to accompany the introduction of new technologies in order to maintain control and use of REE that are essential in their products. This is a production system where the waste or by-product from one process or product is used in the manufacture of another. Honda and Toyota have developed effective return and refining programmes alongside the introduction of their hybrid vehicles which use significant quantities of Nickel-metal-hydride batteries. Every battery is tagged and the customer receives $200 when it is returned at the end of its life. However, the volume of end-of-life batteries being returned will not increase substantially until well into the next decade as the batteries having long life expectancies (Burns, 2009). Toyota also owns a company with an interest in a REE mine being developed in Vietnam. This illustrates how product manufacturers are becoming increasingly interested in the complete life cycle of a product, from access to raw materials through to recycling and recovery of waste and end-of-life products (Lifton, 2009c).

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[79] LCD: liquid crystal display.

Research at the University of Leeds has identified a method of recovering REE from recycling titanium dioxide (TiO_2) waste. The purpose of this study was to eliminate dangerous waste from processing and to improve energy efficiency in TiO_2 extraction. However, it was discovered that significant amounts of neodymium, cerium and lanthanum oxides could be recovered. It has been suggested that if the process could be expanded to a commercial scale it could solve the potential REE shortage (Industrial Minerals, 2009e).

Focus on Britain

There has been no systematic, comprehensive evaluation of REE resources in Britain. However REE are known to occur in a number of geological settings:

- Nodular monazite in Lower Palaeozoic sedimentary rocks of south-central Wales and Exmoor
- REE-bearing minerals associated with the alkaline intrusive complexes of north-west Scotland
- Various REE bearing minerals from the British Tertiary Igneous Province[80]
- Synchysite and other REE minerals associated with lead-zinc-barytes mineralisation in the Alston Block of the North Pennines (Figure 19).

Most of these are small occurrences with no demonstrated economic potential, although the nodular monazite in Wales is widely distributed with high contents of La and Ce reported in alluvial areas.

Nodular monazite

Monazite nodules are present in the Lower Palaeozoic sedimentary rocks of the Welsh Basin and also occur in certain horizons within the Variscan[81] sedimentary succession of south-west England.

These monazite occurrences were identified by BGS geochemical drainage surveys which showed high levels of REE (>5000 ppm cerium) in panned stream sediment concentrates from Wales and south-west England. These anomalies result from the presence of a distinctive form of nodular monazite. The most extensive area containing high cerium levels is in south-central Wales, from samples collected from catchments draining Ordovician and Silurian sedimentary rocks of the Welsh Basin (Cooper and Read, 1983).

The physical appearance of this type of monazite is very different from normal detrital monazite, which is largely derived from granitic sources. The nodules are grey, flattened, ellipsoidal, 0.05 to 2 mm in diameter with an inclusion fabric which is indistinguishable from that of the host rock (Cooper et al., 1983). The nodules show zonation of light and heavy REE and a strong differentiation between the core and rim of single grains (Read et al., 1987). It is thought that the nodules formed by the migration of REE upwards from turbidite[82] muds into the organic-rich hemipelagic[83] layers where they nucleated and grew during diagenesis and compactional dewatering (Milodowski and Zalaciewicz 1991).

An assessment was undertaken in 1994 to investigate the economic potential of the Welsh nodular monazites. The nodules are low in thorium which increases their economic potential as it reduces the radioactive hazard associated with working them. In addition levels of europium, one of the more valuable HREE, are higher than average for placer deposits. The study concluded that the bedrock deposits, which are the source of the REE, do not contain sufficient monazite to be economic and further work would be required to assess the true potential of the placer concentrations (Smith et al., 1994).

Alkaline igneous rocks

Limited studies have been undertaken to evaluate the REE potential of the Caledonian alkaline igneous intrusions of the north-west Highlands of Scotland. The apatites of the Loch Borralan pyroxenite[84], located in the south-west corner of the Assynt region, were found to contain REE values up to 739 ppm Ce, 1764 ppm Ce and 986 ppm Y associated with up to 2 per cent apatite. 0.7 and 2.5 per cent La+Ce were reported from the Loch Ailsh and Ben Loyal complexes respectively (Shaw and Gunn, 1993).

REE minerals identified in the Ben Loyal area include allanite, ancylite[85], betafite[86] and rhabdophane[87] (Shaw and Gunn, 1993). In addition a hydrated species of monazite has been recorded in miarolitic cavitites[88] within a nordmarkite[89] intrusion. The mode of occurrence suggests

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[80] British Tertiary Igneous Province: Area of the north-west British Isles where intense igneous activity occurred during the Palaeocene and early Eocene (about 63 to 52 Ma) as a result of continental separation and lithospheric attenuation during the early stages of the opening of the North Atlantic.

[81] Variscan: orogeny caused by Late Palaeozoic continental collision between Euramerica (Laurussia) and Gondwana to form the supercontinent of Pangaea.

[82] Turbidite: type of sedimentary rock composed of layered particles that grade upward from coarser to finer sizes and are thought to have originated from ancient turbidity currents in the oceans.

[83] Hemipelagic sediment: deep-sea, muddy sediment formed close to continental margins by the settling of fine particles, in which biogenic material comprises 5–75% of the total volume and more than 40 per cent of the terrigenous material is silt.

[84] Pyroxenite: ultramafic igneous rock consisting essentially of minerals of the pyroxene group.

Prismatic gadolinite-(Y) in a miarolitic cavity within the Northern Arran granite, Strathclyde, Scotland Photograph: Fergus MacTaggart, BGS © NERC.

that the mineral was deposited from a late stage aqueous fluid phase (von Knorring and Dearnly, 1959).

Tertiary granites

Several minor occurrences of REE-bearing minerals have been identified within the granites of the British Tertiary Igneous Province, an area of the north-west British Isles where intense igneous activity occurred during the Palaeocene and early Eocene. The Mourne Mountains and Arran granites represent the southern sector of the province with the lower silica Mull and Skye granites making up the northern sector (Hyslop et al., 1999). Fergusonite and gadolinite associated with other REE element-bearing minerals including allanite and zircon have been identified within miarolitic cavities of the northern Arran granite (Hyslop et al., 1999). The fergusonite and gadolinite are found associated with, and growing on, albite and orthoclase. The fergusonite, which occurs as prismatic acicular crystals up to 2 mm long, is dominated by neodymium and yttrium and the gadolinite by yttrium. The gadolinite occurs as dark green, vitreous, turbid, prismatic crystals up to 2.5 mm long (Hyslop et al., 1999).

Gadolinite in addition to an unusual honey-brown coloured type of monazite, has been reported to occur in vugs in the Mourne Mountains granite of Northern Ireland (Hyslop et al., 1999, Green et al., 2005). Three minerals with significant REE content have been identified in the granites of St Kilda, in the Outer Hebrides, allanite, chevkinite[90] and zirkelite[91]. Chevkinite is the most common and can contain up to 41 per cent total REE. However, the REE minerals make up less than one per cent of the host rock (Harding et al., 1982). Various REE-enriched accessory minerals have been identified in the granites of Skye. Allanites and sphenes[92] are particularly LREE enriched with analyses returning an average of 25 and 46 weight per cent REO respectively (Exley, 1980). Gadolinite and kainosite have also been identified in miarolitic cavities within the granites on Skye (Green and McCallum, 2005).

Euhedral crystal of zircon on an albite surface Photograph: Fergus MacTaggart, BGS © NERC.

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[85] Ancylite: hydrated strontium–cerium–carbonate hydroxide. Formula: $SrCe(CO_3)_2(OH) \bullet H_2O$.

[86] Betafite: Calcium Sodium Uranium Titanium Niobium Tantalum Oxide. Formula: $(Ca, Na, U)_2(Ti, Nb, Ta)2O_6(OH, F)$.

[87] Rhabdophane: hydrated neodymium-dominant phosphate. Formula: $(Nd, Ce, La)PO_4 \bullet H_2O$.

[88] Miarolitic cavity: crystal lined irregular cavity or vug most commonly found in granitic pegmatites, but also found in a variety of igneous rocks.

[89] Nordmarkite: A quartz-bearing alkalic syenite that has microperthite as its main component with smaller amounts of oligocase, quartz, and biotite and is characterized by granitic or trachytoid texture.

[90] Chevkinite: cerium–titanium–iron silicate. Formula: $Ce_4(Ti, Fe^{2+}, Fe^{3+})_5O_8(Si_2O_7)_2$.

[91] Zirkelite: titanium–zirconium–iron–yttrium–calcium oxide. Formula: $(Ca,Th, Ce)Zr(Zr, Ti)_2O_7$.

[92] Sphene: calcium–titanium silicate. Formula: $CaTiSiO_5$.

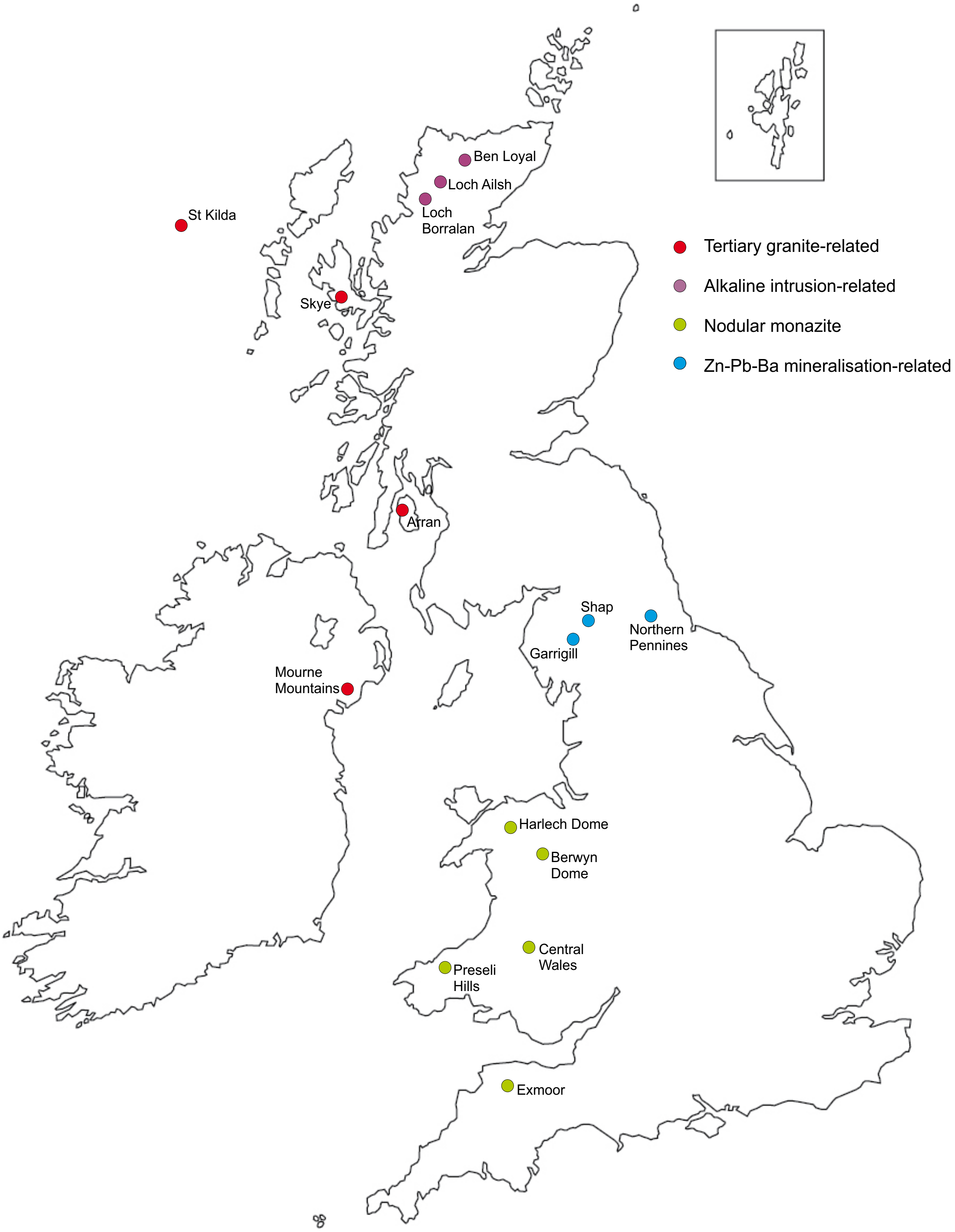

Figure 19 REE mineral occurrences in Britain (Mountain High Map frontiers™ ©1998 Digital Wisdom).

Lead-zinc-fluorite-barite mineralisation

Small quantities of synchysite and other REE minerals have been identified associated with lead-zinc-fluorite-barite mineralisation in the Northern Pennine Orefield of the Alston Block. Bismuthinite-bearing quartz veins near Stanhope and Rookhope contain synchysite, and more rarely monazite, xenotime and adularia, intergrown with bismuthinite (Ixer et al., 1996). Synchysite has also been identified at the Tynebottom Mine, near Garrigill. The synchysite is associated with an assemblage which is believed to be part of the earliest, highest temperature mineralisation of the Alston Block (Ixer and Stanley, 1987).

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This commodity profile was produced by the
British Geological Survey (2010).

It was compiled by Abigail Walters and Paul Lusty
with the assistance of Claire Chetwyn
and Amanda Hill.

This report is one of a series of Commodity Profiles
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