



CHAPTER ONE

WHAT ARE RARE-EARTH ELEMENTS?

1.1. INTRODUCTION

The rare-earth elements (REE) are a group of seventeen speciality metals that form the largest chemically coherent group in the Periodic Table of the Elements¹ (Haxel et al., 2005). The lanthanide series of inner-transition metals with atomic numbers ranging from 57 to 71 is located on the second bottom row of the periodic table (Fig. 1.1). The lanthanide series of elements are often displayed in an expanded field at the base of the table directly above the actinide series of elements. In order of increasing atomic number the REE are: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Scandium (Sc) and yttrium (Y), which have properties similar to the lanthanide series of elements, have atomic numbers of 21 and 39, respectively, and occur above the lanthanides in the Periodic Table of Elements (Fig. 1.1; Appendix 2).

REE are variously referred to as ‘rare-earth metals’ (REM), ‘rare earths’ (RE), ‘rare-earth oxides’ (REO), and ‘total rare-earth oxides’ (TREO). Such phrases as ‘vitamins for industry’, ‘elements of the future’, and ‘21st century gold’ that are often used in the media today reflect their increasing strategic importance for many industrial applications. During recent times there has been much controversy about the actual number of elements included in the REE group. This has ranged from fifteen to eighteen elements. One of the world’s leading authorities on chemical nomenclature and terminology, the International Union of Pure and Applied Chemistry (IUPAC: http://old.iupac.org/dhtml_home.html), has defined the REE as a group of seventeen chemically similar metallic elements that comprise the fifteen lanthanide elements (lanthanum to lutetium), scandium (Sc), and yttrium (Y). The

latter two elements are classified as REE because of their similar physical and chemical properties to the lanthanides, and they are commonly associated with these elements in many ore deposits. Chemically, yttrium resembles the lanthanide metals more closely than its neighbor in the periodic table, scandium, and if its physical properties were plotted against atomic number then it would have an apparent number of 64.5 to 67.5, placing it between the lanthanides gadolinium and erbium. Some investigators who want to emphasise the lanthanide connection of the REE group, use the prefix ‘lanthanide’ (e.g., lanthanide REE: see Chapter 2). In some classifications, the second element of the actinide series, thorium (Th: Mernagh and Mieztis, 2008), is also included in the REE group, while promethium (Pm), which is a radioactive element not found in nature, is sometimes excluded. This particular review will follow the general guidelines recommended by the IUPAC with the REE defined by the fifteen lanthanide elements and the two closely related elements, scandium and yttrium. Thorium is excluded from, and promethium is included in, the final group of seventeen REE described in this report.

The fifteen lanthanide elements have been further subdivided by the British Geological Survey (Walters et al., 2010) into the:

1. light-rare-earth elements (LREE)—lanthanum, cerium, praseodymium, neodymium, promethium, samarium, and europium; and
2. heavy-rare-earth elements (HREE)—gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

In some classifications the more transitional elements samarium and europium may occur in either the LREE or the HREE subgroups. Despite its low atomic weight, yttrium (and scandium) is included with the HREE subgroup because its occurrence, ionic radius, and behavioural properties are closer to the HREE than

¹ Technical terms are explained in Appendix 1.

to the LREE (Cooper, 1990). The LREE are generally more abundant, and less valuable than the HREE. Furthermore, REE with even atomic numbers are more abundant than their neighbours of odd atomic numbers because of their greater relative stabilities of atomic nuclei. Consequently, abundance plots for the REE show zig-zag distribution trends (Fig. 1.2).

Other classifications further divide the REE into Middle REE (MREE) comprising Sm, Eu, Gd, Tb, and Dy, with the remainder of the elements from Ho to Lu, referred to as the HREE. This more detailed subdivision is generally not universally accepted, and in this report they are briefly described in Chapter 2.

The REE share many common physical and chemical properties that make them difficult to distinguish from each other or chemically separate. Such common properties include: silver, silvery-white, and grey metallic colours; soft, malleable, and ductile behaviours; high lustres, which readily tarnish in air; high electrical conductivities; reactive states (to form REO) especially at high temperatures; very small differences in solubility and complex formation between the REE; and dominant oxidation valence state of +3 when the REE are associated with non-metals (although europium has a valence state of +2 and cerium +4). The major physical and chemical properties of the REE are summarised in Table 1.1.

Table 1.1. Major physical and chemical properties of the rare-earth elements (modified from Gupta and Krishnamurthy, 2005; and other sources).

Element	Symbol	Atomic number	Atomic weight	Density (gcm ⁻³) ¹	Melting point (°C) ¹	Boiling point (°C) ¹	Crustal abundance (ppm) ²	Vicker's hardness ³	Crystal structure ^{1,4}
Scandium	Sc	21	44.95	2.989	1541	2832	8	85	Hex
Yttrium	Y	39	88.90	4.469	1522	3337	30	38	Hex
<i>Light-rare-earth elements</i>									
Lanthanum	La	57	138.90	6.146	918	3469	30	37	Hex
Cerium	Ce	58	140.11	8.160	789	3257	60	24	Cub
Praseodymium	Pr	59	140.90	6.773	931	3127	7	37	Hex
Neodymium	Nd	60	144.24	7.008	1021	3127	25	35	Hex
Promethium ⁵	Pm	61	145.00	7.264	1042	3000	4.5 x 10 ⁻²⁰	-	Hex
Samarium	Sm	62	150.36	7.520	1074	1900	5	45	Rho
Europium	Eu	63	151.96	5.244	822	1597	1	17	Cub
<i>Heavy-rare-earth elements</i>									
Gadolinium	Gd	64	157.25	7.901	1313	3233	4	57	Hex
Terbium	Tb	65	158.92	8.230	1356	3041	0.7	46	Hex
Dysprosium	Dy	66	162.50	8.551	1412	2562	3.5	42	Hex
Holmium	Ho	67	164.93	8.795	1474	2720	0.8	42	Hex
Erbium	Er	68	167.26	9.066	1529	2510	2.3	44	Hex
Thulium	Tm	69	168.93	9.321	1545	1727	0.32	48	Hex
Ytterbium	Yb	70	173.04	6.966	819	1466	2.2	21	Cub
Lutetium	Lu	71	174.97	9.841	1663	3315	0.4	77	Hex

¹ Source of data: Periodic Table of the Elements (<http://www.chemicalelements.com/show/dateofdiscovery.html>, and <http://education.jlab.org/itselemental/>).

² Crustal abundances in parts per million (ppm) from Christie et al. (1998).

³ 10 kg load, kg/mm².

⁴ Crystal structure abbreviations: Hex = hexagonal; Cub = cubic; Rho = rhombohedral.

⁵ Rarest REE that is radioactive and has no long-lived or stable isotopes.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be																
3	11 Na	12 Mg																
4	19 K	20 Ca																
5	37 Rb	38 Sr																
6	55 Cs	56 Ba																
7	87 Fr	88 Ra																

Metals										Non-metals								
Alkali	Alkaline earth	Lanthanides			Transition	Post-Transition	Metalloids	Other non-metals	Halogens	Noble gases								
		Actinides																

Rare-Earth Elements

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn									
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd									
57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg									
89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn									

* **

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

* **

Rare-Earth Elements

11-5206

Figure 1.1. Periodic Table of Elements. The seventeen rare-earth elements as defined in this review are indicated in blue font and are contained within a red box. Modified from Dayh (1997).

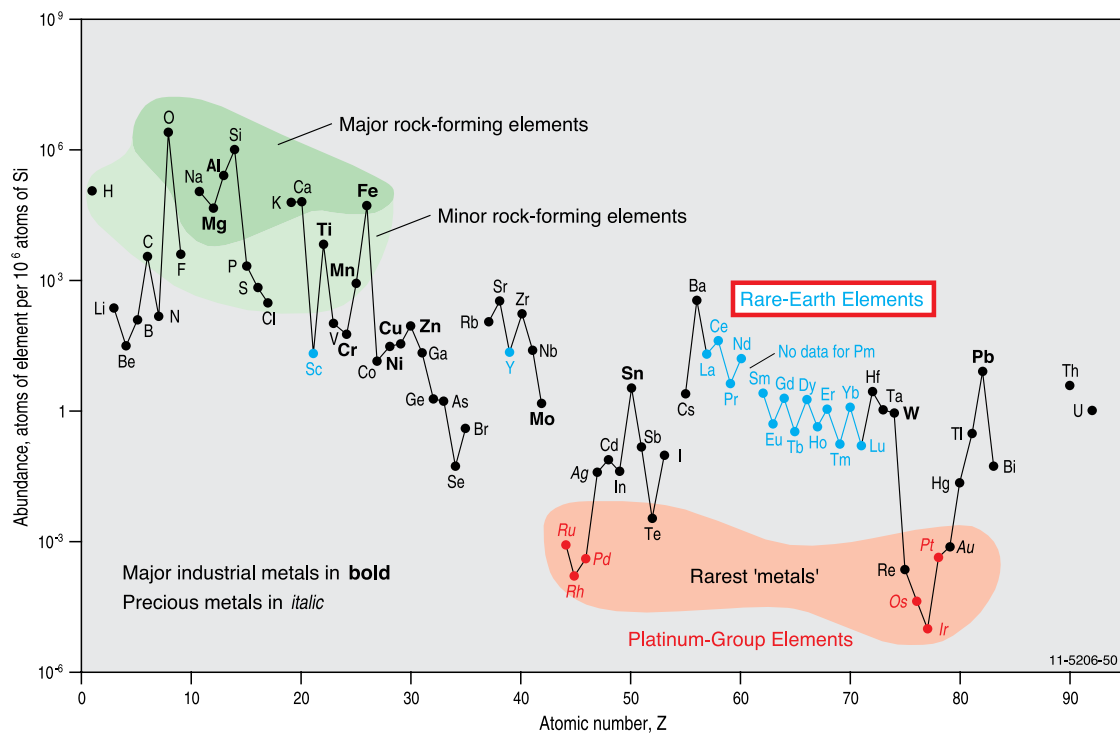


Figure 1.2. Abundances (atom fractions) of the chemical elements in Earth's upper continental crust in reference to atomic number. Many of the elements are grouped into: (1) Rare-Earth Elements (blue font); (2) Major and Minor rock-forming elements (dark and light green fields); (3) Rarest metals (orange field); and Platinum-Group Elements (red font). Modified from Haxel et al. (2005).

Rare-earth elements do not occur as free metals in the Earth's crust, such that all naturally occurring minerals consist of mixtures of various REE and non-metals. Bastnäsite [(Ce,La)(CO₃)F], monazite [(Ce,La,Nd,Th)PO₄], and xenotime (YPO₄) are the three most economically significant minerals of the 200 plus minerals known to contain essential or significant REE (Christie et al., 1998). The chemical compositions and discovery dates of some of the more common REE-bearing minerals are shown in Table 1.2².

Bastnäsite and monazite are principal sources of the LREE, which account for about 95% of the REE utilised (Cooper, 1990). Bastnäsite is named from the Swedish village of Bastnäs, where cerium ore was mined in the late 1800s. It is a fluoro-carbonate of cerium metals containing 60 to 70% REO including lanthanum and neodymium. Bastnäsite has been mined at the large Mountain Pass REE deposit in California, and China has vast bastnäsite deposits that exceed all the other known bastnäsite deposits. Monazite is a cerium, lanthanum, neodymium, and yttrium-bearing phosphate containing 50 to 78% REO. Monazite is also the principal ore of thorium, containing up to 30% thorium, which together with smaller quantities of uranium (up to 1%) imparts radioactive properties to the monazite. Xenotime is a yttrium-bearing phosphate hosting 54 to 65% REO, and comprising other REE such as erbium and cerium, and thorium. Xenotime and minerals such as allanite are common sources of the HREE and yttrium.

Bastnäsite occurs predominantly in calc-silicate rich rocks related to alkaline intrusive igneous complexes, in particular carbonatite, dolomitic breccia with syenite intrusives, pegmatite, and amphibolite skarn. Monazite and xenotime are more common as accessory minerals in low-calcium granitic rocks, gneisses, pegmatites, and aplites. Xenotime is commonly associated with zircon and can enclose that mineral. Following weathering of granites and pegmatites, monazite and xenotime are concentrated in heavy mineral placer deposits because of their resistance to chemical attack and high specific gravities.

Other commercial sources of REE are apatite and loparite (western Russia), REE-bearing clays ('Longnan clay' or 'southern ionic clay', Jiangxi Province, China), and various minerals, such as allanite that are produced as a by-product of uranium mining (Canada). Of lesser importance are zircon (Th, Y, and Ce) and euxenite. One of the major commercial sources of scandium is as a by-product from the processing of uranium and tungsten.

Some of the most common REE-bearing minerals are compiled in Table 1.2. The majority of these minerals were discovered in Europe (Russia, Norway, Sweden, Greenland, Germany), with some occurrences recorded from the USA, India, Brazil, Colombia, and Sri Lanka. Many other REE-bearing minerals that have been approved by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) can be found in Mandarino (1999). The minerals shown in Table 1.2 have been approved by the CNMMN.

Table 1.2. Rare-earth-element-bearing minerals.

Mineral	Mineral chemistry	wt % REO	Discovered ¹
Aeschnynite	(Ce,Ca,Fe,Th)(Ti,Nb) ₂ (O,OH) ₆	36	Norway; Ural Mountains, Russia
Allanite (orthite)	(Ce,Ca,Y) ₂ (Al,Fe) ₃ (SiO ₄) ₃ (OH)	3 to 51	1810: Aluk Island, Greenland
Anatase	(Ti,REE)O ₂	3	1801: St Christophe-en-Oisans, France
Ancylite-(Ce)	SrCe(CO ₃) ₂ (OH)•H ₂ O	46 to 53	1899: Narssârssuk, Narsaq, Greenland
Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	19	Bronze Age (3300–1200 BC); widespread
Bastnäsite-(Ce)²	(Ce,La)(CO ₃)F	70 to 74	1838: Bastnäs mine, Västmanland, Sweden
Brannerite	(U,Ca,Y,Ce)(Ti,Fe) ₂ O ₆	6	1920: Kelly Gulch, Stanley, Idaho, USA
Britholite-(Ce)	(Ce,Ca) ₂ (SiO ₄) ₃ (OH,F)	56	1901: Nauyasakik, Narsaq, Greenland
Brockite	(Ca,Th,Ce)(PO ₄)•H ₂ O		1962: Bassick mine, Colorado, USA
Calcio-ancylite (Ce)	(Ca,Sr)Ce ₃ (CO ₃) ₄ (OH) ₃ •H ₂ O	60	Kola Peninsula, Russia
Cerianite-(Ce)	(Ce ⁴⁺ ,Th)O ₂	81	1955: Firetown, Sudbury, Ontario, Canada
Cerite-(Ce)	Ce ₉ ³⁺ Fe ³⁺ (SiO ₄) ₆ [SiO ₃ (OH)](OH) ₃	60	1751: Bastnäs mine, Västmanland, Sweden
Cheralite-(Ce)	(Ce,Ca,Th)(P,Si)O ₄	5	Chera, Travancore, India
Chevkinitite	(Ca,Ce,Th) ₄ (Fe ²⁺ ,Mg) ₂ (Ti,Fe ³⁺) ₃ Si ₄ O ₂₂		1839: Ural Mountains, Russia
Churchite-(Y)	YPO ₄ •2H ₂ O	44	1923: Maffei mine, Bavaria, Germany
Crandallite	CaAl ₃ (PO ₄) ₂ (OH) ₅ •H ₂ O		1917: Brooklyn mine, Silver City, Utah, USA

² The reader should refer to Table 1.2 for the chemical compositions of REE-bearing minerals since they will not be repeated throughout this report.

Table 1.2. Rare-earth-element-bearing minerals (continued).

Mineral	Mineral chemistry	wt % REO	Discovered ¹
Doverite (synchysite–Y)	YCaF(CO ₃) ₂		1951: Scrub Oak mine, New Jersey, USA
Eudialyte	Na ₄ (Ca,Ce) ₂ (Fe ²⁺ ,Mn ²⁺ ,Y) ZrSi ₈ O ₂₂ (OH,Cl) ₂	1 to 10	1819: Kangerdluarssuk Firth, Narsaq, Greenland
Euxenite–(Y)	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆	<40	1840: Jølster, Sogn og Fjordane, Norway
Fergusonite–(Ce)	(Ce,La,Y)NbO ₄	47	1806: Kikertaursak, Greenland; Ukraine
Fergusonite–(Y)	YNbO ₄		1826: Kikertaursak, Greenland
Florencite–(Ce)	CeAl ₃ (PO ₄) ₂ (OH) ₆	32	pre-1951: Mata dos Criolos, Minas Gerais, Brazil
Florencite–(La)	(La,Ce)Al ₃ (PO ₄) ₂ (OH) ₆		pre-1980: Shituru mine, Congo (Zaire), Africa
Fluocerite–(Ce)	(Ce,La)F ₃		1845: Broddbo and Finnbo, Dalarna, Sweden
Fluocerite–(La)	(La,Ce)F ₃		1969: Zhanuzak, Kazakhstan
Fluorapatite–(Ce)	(Ca,Ce) ₅ (PO ₄) ₃ F	0 to 21	1860: Greifenstein Rocks, Saxony, Germany
Fluorite	(Ca,REE)F ₂		1530: England; Czech Republic; Germany
Gadolinite	(Ce,La,Nd,Y) ₂ Fe ²⁺ Be ₂ Si ₂ O ₁₀	40	1788: Ytterby mine, Resarö, Sweden
Gagarinite–(Y)	NaCaY(F,Cl) ₆		pre-1961: Akzhaylyautas Mountains, Kazakhstan
Gerenite–(Y)	(Ca,Na) ₂ (YREE) ₃ Si ₆ O ₁₈ •2H ₂ O		1998: Strange Lake, Quebec–Labrador, Canada
Gorceixite	(Ba,REE)Al ₃ (PO ₄)(PO ₃ OH)(OH) ₆		1906: Ouro Preto, Minas Gerais, Brazil
Goyazite	SrAl ₃ (PO ₄) ₂ (OH) ₅ •H ₂ O		1884: Diamantina, Minas Gerais, Brazil
Hingganite–(Y)	(Y,Yb,Er) ₂ Be ₂ Si ₂ O ₈ (OH) ₂		1984: Greater Hinggan Mountains, China
Huanghoite–(Ce)	BaCe(CO ₃) ₂ F	38	1960s: Bayan Obo deposit, Inner Mongolia
Hydroxylbastnäsite–(Ce)	(Ce,La)(CO ₃)(OH,F)	75	Kola Peninsula and Ural Mountains, Russia
Ilmorite–(Y)	Y ₂ (SiO ₄)(CO ₃)		pre-1970: Honshu Island, Japan
Kainosite–(Y)	Ca ₂ (Y,Ce) ₂ Si ₄ O ₁₂ (CO ₃)•H ₂ O	38	1885: Hidra, Vest-Agder, Norway
Loparite–(Ce)	(Ce,Na,Ca)(Ti,Nb)O ₃	32 to 34	1925: Maly Mannepakhk, Kola Peninsula, Russia
Monazite–(Ce)	(Ce,La,Nd,Th)PO ₄	35 to 71	1823: Ilmen Mountains, Ural Mountains, Russia
Mosandrite	(Na,Ca,Ce) ₂ Ti(SiO ₄) ₂ F	<65	1841: Låven Island, Larvik, Norway
Parisite–(Ce)	Ca(Ce,La) ₂ (CO ₃) ₃ F ₂	59	Muzo mine, Colombia
Perovskite	(Ca,REE)TiO ₃	≤37	1839: Achmatovsk mine, Ural Mountains, Russia
Pyrochlore	(Ca,Na,REE) ₂ Nb ₂ O ₆ (OH,F)		1826: Stavern, Larvik, Vestfold, Norway
Rhabdophane–(Ce)	(Ce,La)PO ₄ •H ₂ O		pre-1992: Fowey Consols, Cornwall, England
Rhabdophane–(La)	(La,Ce)PO ₄ •H ₂ O		1883: Salisbury Iron mines, Connecticut, USA
Rinkite	(Ca,Ce) ₄ Na(Na,Ca) ₂ Ti(Si ₂ O ₇) ₂ (O,F) ₂		1884: Kangerdluarssuk, Narsaq, Greenland
Samarskite–(Y)	(Y,Ce,U,Fe ³⁺) ₃ (Nb,Ta,Ti) ₅ O ₁₆	12	1839: Blyumovskaya pit, Ural Mountains, Russia
Steenstrupine–(Ce)	Na ₁₄ Ce ₆ Mn ²⁺ Mn ³⁺ Fe ₂ ²⁺ (Zr,Th) (Si ₆ O _{18/2}) ₂ (PO ₄) ₇ •3H ₂ O		1853–54: Kangerdluarssuk, Narsaq, Greenland
Synchysite–(Ce)	Ca(Ce,La)(CO ₃) ₂ F	49 to 52	1953: Narsarsuk, Greenland
Thalénite–(Y)	Y ₃ Si ₃ O ₁₀ (OH)	63	Österby, Dalarna, Sweden
Titanite (sphene)	(Ca,REE)TiSiO ₅	≤3	1795: Hauzenberg, Bavaria, Germany
Uraninite	(U,Th,Ce)O ₂		1772: Jáchymov, Bohemia, Czech Republic
Vitusite–(Ce)	Na ₃ (Ce,La,Nd)(PO ₄) ₂		1980: Kola Peninsula, Russia; Narsaq, Greenland
Xenotime–(Y)	YPO ₄	52 to 67	1824: Ytterby mine, Sweden; Hidra, Norway
Yttrifluorite	(Ca,Y)F ₂		1911: Hundholmen, Tysfjord, Norway
Yttrotantalite–(Y)	(Y,U,Fe ²⁺)(Ta,Nb)O ₄	<24	Ytterby mine, Resarö, Sweden
Zircon	(Zr,REE)SiO ₄	<5	1783: Sri Lanka; 1789: Germany

Source of information: Habashi (1994); Long et al. (2010); mindat.org (<http://www.mindat.org/index.php>); and reproduced with permission, and modified, from Tasman Metals Limited (<http://www.tasmanmetals.com/s/OresMinerals.asp>).

¹ Estimated year of mineral discovery; discovery location, and/or type location of mineral occurrence.

² Minerals shown in bold have historically been processed to recover rare-earth elements.

Other minor REE-bearing minerals shown in this report, and not listed in this table, will have their chemical compositions shown in parenthesis in the text.

It is well established that REE are not rare, nor are they earth, as their name implies. The term ‘rare earths’ dates back to the 18th and 19th centuries, when many of the REE were considered ‘rare’ in the Earth’s crust at the time they were first identified (mostly in Europe), and ‘earths’ because as oxides they have an earthy appearance and resemble such materials as lime, alumina, and magnesia. Despite their name, some of the REE are more common than gold, silver, and the platinum-group elements (PGEs), while cerium, yttrium, and lanthanum are more abundant than lead, tin, and uranium (Fig. 1.2). Chemically, the REE are so similar that over billions of years the individual elements (except scandium) have not been separated in nature (Cooper, 1990). The prominent 19th century British chemist and physicist, Sir William Crookes (1832–1919), stated that, *“rare earth elements perplex us in our researches, baffle us in our speculations and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying and murmuring strange revelations and possibilities”*. The REE are not easy elements to isolate or to understand, and consequently there was often a very long lag time between the discovery of the individual REE and the determination of its chemical attributes and practical uses. For example, many REE were discovered in the ~1880s, but their detailed chemical attributes and applications were only defined many decades later. The fact that many REE occur together in the same mineral or rock provided further complications for their accurate identification. Such mineral hosts include monazite [(Ce,La,Th,Nd,Y)PO₄], loparite (Na,Ce,Ca)₂(Ti,Nb)₂O₆, bastnäsite [(Ce,La,Y)CO₃F], and lateritic ion-adsorption clays. Industries during these early times did not initially attempt to separate the individual REE, instead they used them in a blended hybrid metal alloy called ‘misch’ metal (German for mixed metal). In 1891, ‘misch’ metal provided one of the first commercial applications for REE, when it was used as an ingredient in lamp mantles. Such lamps were hung above open flames, where they burned and produced a bright white light. The industrial uses of the REE were not fully realised until the early 1960s when efficient separation techniques, such as ion exchange, fractional crystallisation, and liquid-liquid extraction, were developed.

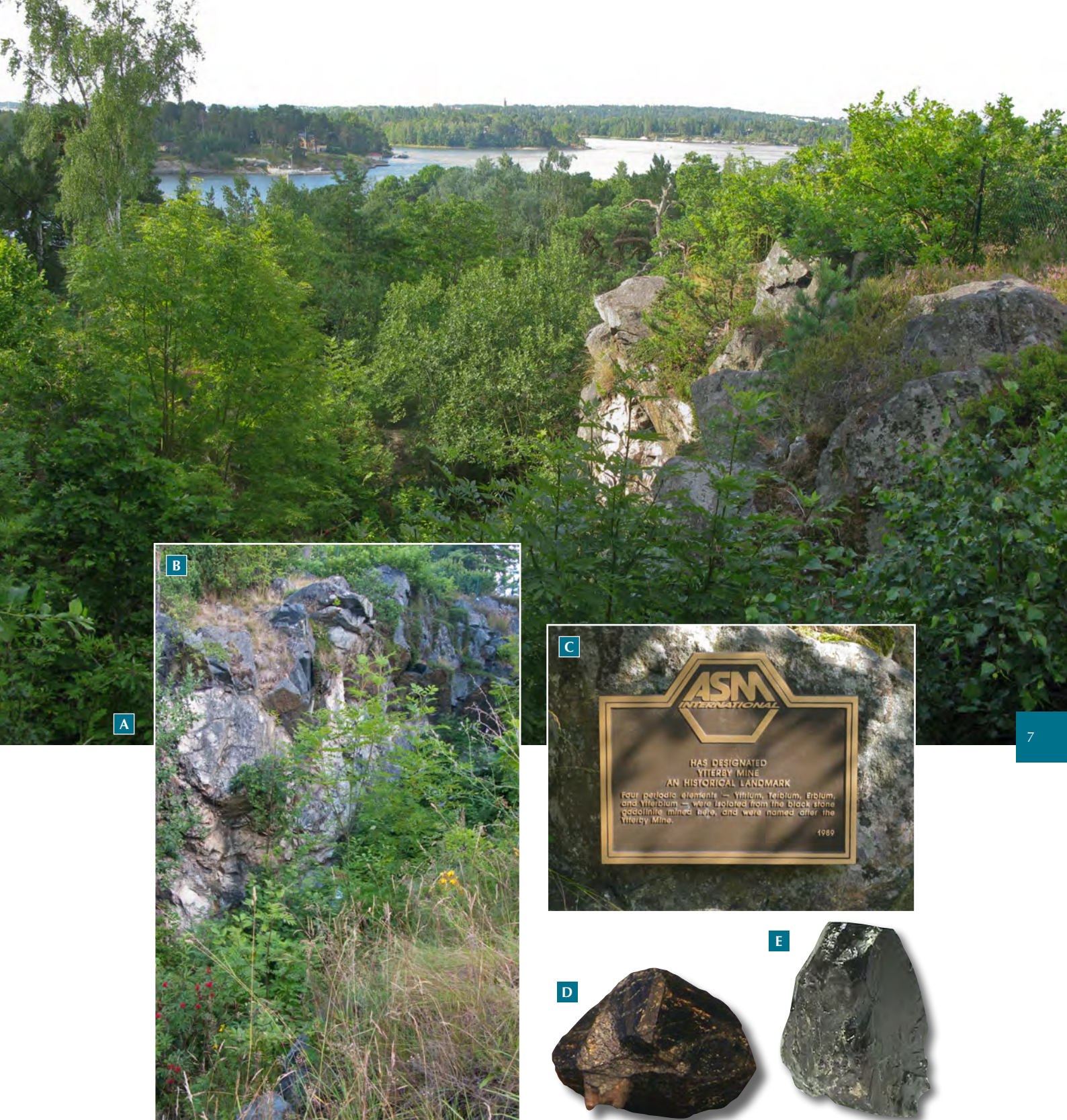
1.2. DISCOVERY AND ETYMOLOGY

In 1751, the Swedish mineralogist and chemist, Baron Axel Fredrik Cronstedt (1722–1765) is credited with the first discovery of a mineral containing REE. Cronstedt, who also discovered nickel in the same

year, described the heavy stone from the Bastnäs mine in Sweden, as ‘Bastnäs tungsten’. It was not until 1803, that a group of Swedish and German chemists independently isolated and confirmed the rare-earth component of the heavy stone and called it cerium oxide, and the mineral they called cerite to honour the newly found small planet ceres (Habashi, 1994).

However, it was the discovery in 1787 of an unusually heavy greenish black rock in a small feldspar-bearing quarry near the village of Ytterby, on the island of Resarö near Stockholm in Sweden, that represents the seminal event in the identification record of the REE (Fig. 1.3A–E). This small quarry was originally mined in the 1500s for ironwork, and later in the 1700s feldspar was obtained for porcelain and the manufacture of glass. The unusual dark rock was found by amateur mineralogist Lieutenant Carl Axel Arrhenius (1757–1824), who named it ytterbite, after the local village. A few years later in 1794, the distinctive black rock was analysed by Johan Gadolin (1760–1852), a Finnish professor of chemistry at the University of Åbo in Finland. Gadolin determined that it contained a new element to be called yttrium. It was some fifty years later, that Swedish chemist Carl Gustav Mosander (1797–1858) found two other non-pure elements, terbium and erbium, were associated with the yttrium. The famous black rock from the dumps of the Ytterby quarry comprised 38% of new ‘earth type’ (‘earths’ are compounds of elements, usually oxides; hence the name rare-earth elements). After more than 100 years of research by many prominent European chemists, it was eventually shown that Arrhenius’s original black rock sample contained at least ten new rare-earth elements that became known as dysprosium, erbium, gadolinium, holmium, lutetium, scandium, terbium, thulium, ytterbium, and yttrium. In recognition of John Gadolin’s efforts of being the first person to isolate a REE, the unusual Ytterby mineral was renamed by German chemist Martin Klaproth (1743–1817) as gadolinite [(Ce,La,Nd,Y)₂FeBe₂Si₂O₁₀].

The seventeen members of the REE group were discovered between 1794 and 1945, with the majority (14) of the elements found in the nineteenth century. The four decades between 1870 and 1910 were the most productive period accounting for the reliable identification of eleven REE. The radioactive element promethium, which has no stable isotopes and is artificially produced, was the last REE to be ‘found’ in 1945. Most of the REE identified during the eighteenth and nineteenth centuries were named in recognition of the scientist who found them or defined their elemental properties. Several European chemists



Figures 1.3A–E. The discovery in 1787 of the mineral gadolinite near the village of Ytterby in Sweden was a seminal event in the identification record of the rare-earth elements. The images in this figure are from this historic site.

A. Panoramic view from the Ytterby rare-earth-element mine, Resarö, Sweden. Rare-earth elements were first isolated from the mineral gadolinite found near the village of Ytterby.

B. Close-up of the Ytterby rare-earth-element-mine.

C. Plaque that denotes the significance of the Ytterby rare-earth-element occurrence.

D–E. Gadolinite specimens from the Ytterby mine, Sweden. The specimen shown in D is 2 cm across and has well-developed crystal faces, whereas the fractured sample shown in E is 1.8 cm in size and has a high lustre and vitreous appearance.

Images A to C are reproduced with permission from Peter van der Krogt, <http://elements.vanderkrogt.net/Ytterby/index.html>

Images D and E are reproduced with permission from John Veevaert, <http://trinityminerals.com/ms2003/day3.shtml> and http://www.rareterra.com/cgi-bin/rareminerals/specimen.cgi?Specimen_Code=RG808&Specimen_Name_Starts=

and mineralogists, in particular from France, Sweden, Switzerland, and Germany, were instrumental in successfully isolating and identifying the REE (Table 1.3 and Fig. 1.4). Some of the REE were also named from their geographical source location, from Greek or Latin references and their mythical context, and from the person finding the original REE-bearing mineral rather than the scientist who isolated the element.

The discovery history of the REE highlights one hundred and fifty years of scientific endeavours, elaborate and laborious experimental trials, and frustrating analytical confusion. This protracted evolutionary record commenced before the time of Dalton's determination of atomic weight values, the development of the Periodic Table of Elements, the advent of optical spectroscopy, Bohr's theory of the electronic structure of atoms, and Moseley's x-ray detection method for atomic number determinations (Holden, 2004). The similar chemical properties of the REE made them difficult to chemically isolate and consequently many mixtures of elements were mistaken for elemental species. Other factors that hindered the accurate identification of the REE were the lack of spectral analysis and reliable atomic weight data for the elements. The fifteen elements of the lanthanide group have a narrow range of atomic weights that sequentially increase from 138.90 for lanthanum to 174.97 for lutetium (Table 1.1). Only scandium (atomic weight of 44.95) and yttrium (88.90), have atomic weights significantly different from the lanthanide group. Consequently, during these early explorative years, many erroneous species were named, including: austrium, berzelium, carolinium, celtium, columbium, damarium, decipium, demonium, denebium, didymium, donarium, dubhium, eurosamarium, euxenium, glaucodymium, incognitium, ionium, junonium, kosmium, lucium, metacerium, monium, mosandium, moseleyum, mssrium, neokosmium, nipponium, philippium, rogerium, russium, sirium, thornine, vestium, victorium, wasmium, and welsium. Three important developments that assisted with the resolution of this confusion were the production of very pure REE samples, the discovery of spectroscopic analysis in 1859, and the introduction of the Periodic Table of Elements (Fig. 1.1) in 1869.

The following summary of the discovery and derivation of names relating to the REE is in part from: History of the Origin of the Chemical Elements and their Discoverers by Holden (2004: <http://www.nndc.bnl.gov/content/elements.html>); Elementymology & Elements Multidict by Krogt (2011: <http://elements.vanderkrogt.net/>); the Thomas Jefferson National Accelerator Facility (reproduced with permission)–

Office of Science Education (<http://www.jlab.org/> and <http://education.jlab.org/itselemental/>); The Lanthanides (http://www.angelo.edu/faculty/kboudrea/periodic/trans_lanthanides.htm); and Habashi (1994). The REE in the following section are discussed in order of increasing atomic number (Z), commencing with scandium (atomic number of 21) and ending with lutetium (71). Table 1.3 provides a chronological summary of the discovery record of the rare-earth elements.

Scandium (Sc; Atomic Number (Z) = 21): Scandium derives its name from the Latin *scandia* for 'Scandinavia' where scandium-bearing minerals were found. It is never found free in nature, with its direct commercial sources being unusual REE-bearing minerals. Scandium was the first element whose discovery was predicted using the Periodic Table of the Elements. The existence of scandium was predicted nearly ten years before it was actually discovered. The prediction was made by Russian chemist Dmitri Mendeleev (1834–1907), who developed the Periodic Table of Elements based on his periodic law. The table originally contained a number of empty boxes for elements that had not been discovered. Chemists were able to search for these elements based on the properties of the elements around the empty boxes. Scandium was eventually discovered in 1879 by Lars Fredrik Nilson (1840–1899), a Swedish chemist, while attempting to produce a sample of pure ytterbia from 10 kilograms of the mineral euxenite [(Y,Ca,Er,La,Ce,U,Th)(Nb,Ta,Ti)₂O₆] from Scandinavia. The substance discovered using spectral analysis by Nilson was not pure scandium metal, but scandium oxide (Sc₂O₃). It is difficult to produce pure scandium metal from scandium oxide. Metallic scandium was produced for the first time in 1937.

Yttrium (Y; Z = 39): Yttrium was the first of the so-called REE discovered. It was discovered by Finnish chemist Johan Gadolin in 1794, while analysing the mineral gadolinite [(Ce,La,Nd,Y)₂FeBe₂Si₂O₁₀] from the Swedish village of Ytterby. The name of this element originally given by Gadolin was ytterbium, named after its location, and it was later shortened to yttrium by Anders Gustav Eckberg. Later another element was given the name ytterbium that Gadolin had previously proposed. In 1843, Carl Gustav Mosander (1797–1858), a Swedish professor of chemistry and mineralogy at the Caroline Institute in Stockholm, successfully separated the element.

Lanthanum (La; Z = 57): Lanthanum was discovered in 1839 by Carl Gustaf Mosander. The name was derived from the Greek *lanthana*, that means 'to

lie hidden or to escape notice' because it was an obscure component of cerium ore and it was difficult to separate from that rare-earth material. In 1825, Mosander undertook some separation experiments to prepare cerium sulphide. He became convinced that the refined samples also contained earth oxides. Some ten years later, he carried out further separation procedures and he obtained two oxide samples. For one of these he assigned the name lanthanum and for the other he used the name didymium (or twin). Lanthanum was eventually isolated in relatively pure form in 1923. Today, lanthanum is primarily obtained through an ion exchange process from monazite sand $[(\text{Ce}, \text{La}, \text{Th}, \text{Nd}, \text{Y})\text{PO}_4]$, a material rich in REE that can contain as much as 25% lanthanum.

Cerium (Ce; Z = 58): Cerium was discovered in 1803 by Swedish chemist Jöns Jacob Berzelius (1779–1848) and Swedish mineralogist Wilhelm von Hisinger (1766–1852), and also independently by German chemist Martin Heinrich Klaproth (1743–1817). Cerium was originally named cererium, but was shortened to cerium, after the dwarf planet Ceres discovered by Italian astronomer Giuseppe Piazzi in 1801, and named for Ceres, the Roman goddess of agriculture. Klaproth called the new element ochroite because of its yellow colour. It was first chemically isolated in 1875 by the American mineralogist and chemist William Frances Hillebrand (1853–1925) and the American chemist Thomas Norton.

Praseodymium (Pr; Z = 59): The name was originally praseodidymium that was subsequently shortened to praseodymium, which is derived from the Greek *prasios* for 'green' and *didymos* for 'twin' because of its pale green salts and its resemblance to another closely related REE, lanthanum. Praseodymium was discovered in 1885 by Austrian chemist Carl Auer von Welsbach (1858–1929). He separated praseodymium, as well as the element neodymium, from a material known as didymium. The first enduring commercial use of 'purified' praseodymium, which was first investigated in the late 1920s and continues today, is in the form of a yellow-orange stain for ceramics, 'Praseodymium Yellow'.

Neodymium (Nd; Z = 60): The name was originally neodidymium and was later shortened to neodymium, which is derived from the Greek *neos* for 'new-one' and *didymos* for 'twin'. Neodymium was discovered in 1885 by Carl Auer von Welsbach during fractional crystallisation procedures that involved the separation of praseodymium from the material didymium. Its identification was confirmed by spectroscopic analysis. However, it was not isolated in relatively pure form

until 1925, and the first large-scale commercial production of neodymium commenced in the 1950s. High purity (above 99%) neodymium was initially obtained through an ion-exchange process from monazite, but in more recent times most neodymium is extracted from bastnäsite and purified by solvent extraction.

Promethium (Pm; Z = 61): Promethium was the last of the seventeen REE discovered. Its existence was predicted by Czech chemist Bohuslav Brauner (1855–1935) in 1902, but it was not until 1947 that its discovery was confirmed. Promethium is a radioactive metal that has never been found on the Earth's surface; it has only been prepared artificially in particle accelerators and in other unusual reactions. The longest lived isotope of promethium has a short life of less than 20 years and it only exists in nature in negligible amounts (i.e., about 570 g in the entire Earth's crust). Brauner expanded Mendeleev's Periodic Table of the Elements by extending it past lanthanum, and he also predicted the existence of a new element located between neodymium and samarium. The name promethium is derived from the mythical Greek god figure 'Prometheus' who stole fire from heaven and gave it to mankind, and was subsequently punished. Several groups claimed to have produced the element, but they could not confirm their discoveries because of the difficulty of separating promethium from other elements. There were claims of discovery of such an element called Florentium in Italy in 1924, and at the University of Illinois, USA, in 1926, where the new element was named illinium. It was later found that these new 'elements' did not exist in nature and both claims were subsequently discarded. In 1941, neodymium and praseodymium were irradiated with neutrons, deuterons and alpha particles at the Ohio State University in the USA and new activities were recorded. It was determined some of these activities were associated with promethium. However, no chemical proof of promethium was available because the REE could not be separated from each other at that time. The break through came in the mid-1940s from a group of American chemists working on the Manhattan Project in Tennessee which was aimed at creating fuel for the atomic bomb. Promethium was first synthesised and identified in 1945 (confirmed in 1947) in fission products from the thermal neutron fission of U^{235} at the Clinton (later Oak Ridge National Laboratory, Oak Ridge, Tennessee) laboratory by Charles D. Coryell (1912–1971), Jacob A. Marinsky (b. 1918), and Lawrence E. Glendenin (1918–?). The fission products, Pm^{147} and Pm^{149} were also identified during the slow neutron activation of neodymium.

Samarium (Sm; Z = 62): Samarium derives its name from the mineral samarskite, in which it was found and which had been named after Vasili Samarsky-Bykhovets (1803–1870). Samarsky-Bykhovets was the Chief of Staff of the Russian Corps of Mining Engineers who granted access for German mineralogists to study mineral samples from the Ural Mountains. He became the first person to have a chemical element named after him, albeit indirectly. Detection of samarium and related elements was announced by several scientists in the second half of the 19th century; however, most sources grant this priority to the French chemist Paul Émile Lecoq de Boisbaudran (1838–1912). Samarium was observed spectroscopically by Swiss chemist Jean Charles Galissard de Marignac (1817–1894), professor of Chemistry at the University of Geneva, in the material didymia in 1853. In 1879, Paul Émile Lecoq de Boisbaudran was the first to isolate samarium from the mineral samarskite $[(Y,Ce,U,Fe)_3(Nb,Ta,Ti)_5O_{16}]$.

Europium (Eu; Z = 63): The element is named after the continent of Europe. According to mythology, the continent derives its name from the daughter of the Phoenician King Agenor, who was abducted by Zeus in the shape of a bull. Europium was first found by the French chemist Paul Émile Lecoq de Boisbaudran in 1890, who obtained spectral lines not accounted by the other REE samarium or gadolinium. However, the actual discovery of europium is generally credited to French chemist Eugène-Anatole Demarçay (1852–1904), who suspected samples of the recently discovered element samarium were contaminated with an unknown element in 1896 and who was able to isolate relatively pure europium from magnesium-samarium nitrate in 1901.

Gadolinium (Gd; Z = 64): Gadolinium derives its name from the mineral gadolinite, which in turn was named after the Finnish chemist, physicist, and mineralogist Johan Gadolin. Gadolinite was the first mineral discovered with confirmed concentrations of REE. Gadolinium has the distinction of being the only elemental name derived from Hebrew (*gadol* means 'great'). Spectroscopic evidence for the existence of gadolinium was first observed in 1880 by the Swiss chemist Jean Charles Galissard de Marignac while investigating gadolinite and didymia.

Terbium (Tb; Z = 65): The mineral gadolinite, discovered in a quarry near the village of Ytterby in Sweden has been the source of many REE. The element terbium was named after the Swedish village of Ytterby. In 1843, Carl Gustaf Mosander was able to separate gadolinite into three materials, which he named yttria, erbia, and terbia. As might be expected considering

the similarities between their names and properties, scientists soon confused erbia and terbia and, by 1877, had reversed their names. What Mosander called erbia is now called terbia and visa versa. From these two substances, Mosander discovered two new elements, terbium and erbium. Pure forms of the metal were only isolated with the recent advent of ion exchange techniques.

Dysprosium (Tb; Z = 66): Dysprosium derives its name from the Greek *dysprositos* for 'hard to get at', in regard to the difficulty in separating this REE from an impure holmium oxide through a laborious sequence of dissolution in acid and ammonia. Discovery was first claimed in 1878 by the Swiss chemist Marc Delafontaine in the mineral samarskite and he called it philippia. However, philippia was subsequently found to be a mixture of terbium and erbium. Dysprosium was actually discovered by French chemist Paul Émile Lecoq de Boisbaudran (1838–1912) in 1886, as an impurity in erbia, the oxide of erbium. The grey-white metal was isolated in 1906 by Georges Urbain (1872–1938), another French chemist. Pure samples of dysprosium were first produced much later after the development of ion exchange analytical techniques in the 1950s.

Holmium (Ho; Z = 67): Holmium derives its name from the Latin *holmia* for 'Stockholm'. It was discovered in 1878 by the Swiss chemists Jacques-Louis Soret (1827–1890) and Marc Delafontaine (1837–1911), who noticed aberrant spectrographic absorption bands of a then-unknown element, which they called 'Element X'. Shortly later in 1879, it was independently described by the Swedish chemist Per Theodor Cleve (1840–1905). The three scientists are equally given credit for the element's discovery. It was first isolated in 1911 by chemist Holmberg, who proposed that the name holmium was either to recognise Cleve, who was from Stockholm, or perhaps to establish his own name in history. Cleve used the same chemical method that Carl Gustaf Mosander developed to discover lanthanum, erbium, and terbium, namely investigating the impurities of other REO. He started with erbia, the oxide of erbium (Er_2O_3), and removed all the known contaminants. After further processing, he obtained two new materials, one brown and the other green. Cleve named the brown material holmia, and the green material thulia. Holmia is the oxide of the element holmium and thulia is the oxide of the element thulium.

Erbium (Er; Z = 68): The mineral gadolinite discovered near Ytterby in Sweden has been the source of many REE, including erbium. In 1843, Swedish

chemist Carl Gustaf Mosander separated gadolinite into three materials, which he named yttria, erbia, and terbia. From these substances, Mosander discovered two new elements, terbium and erbium. However, during these early times erbia and terbia were confused. After 1860, terbia was renamed erbia, and after 1877, what had been known as erbia, was renamed terbia. Fairly pure Er_2O_3 was independently isolated in 1905 by chemists Georges Urbain (1872–1938) and Charles James, and pure erbium metal was not produced until 1934.

Thulium (Tm; Z = 69): Thulium derives its name from *Thule*, the earliest Latin name for the northernmost part of the civilised world—‘Scandinavia’ (Norway, Sweden, and Iceland). However, to the ancient Greeks, Thule was simply the northernmost habitable region of the world. The chemical symbol for thulium was initially Tu, but this was changed by the International Commission on Atomic Weights to Tm, since the symbol Tu was at that time used for tungsten (symbol is now W). Thulium was discovered in 1879, when the Swedish chemist Per Theodor Cleve’s was investigating the oxides of the REE. His analytical procedures were similar to the chemical separation methods previously developed by Carl Gustaf Mosander during his discovery of lanthanum, erbium, and terbium. He started with erbia, the oxide of erbium (Er_2O_3), and removed all of the known contaminants. After further processing, Cleve obtained a green product which he named thulia. Thulia is the oxide of the element thulium, which was first isolated in 1911 by the American chemist Charles James. High-purity thulium oxide was first produced commercially in the late 1950s, with the advent of more sophisticated ion-exchange separation technology.

Ytterbium (Yb; Z = 70): Many REE have been derived from the mineral gadolinite found in a quarry near Ytterby in Sweden. The element ytterbium was named after the Swedish village of Ytterby. It was the fourth element named after this village (also yttrium, erbium, and terbium). In 1843, Swedish chemist Carl Gustaf Mosander separated gadolinite into yttria, erbia, and terbia. Jean Charles Galissard de Marignac, French professor of Chemistry at the University of Geneva, discovered in 1878 that erbia consisted of two components. One component was named ytterbia by Marignac, while the other component retained the name erbia. Due to his original understanding of the composition of ytterbia, Marignac is credited with the discovery of ytterbium. Marignac believed that ytterbia was a compound of a new element, which he named ytterbium. Other chemists produced and experimented

with ytterbium in an attempt to determine some of its properties. Unfortunately, the various scientists obtained different results from the same experiments. While some of them interpreted these inconsistent results to be due to poor procedures or faulty equipment, the French chemist Georges Urbain proposed that ytterbium wasn’t an element at all, but a mixture of two elements. In 1907, Urbain was able to separate ytterbium into two elements. He named one of the elements neoytterbium and the other element lutecium. Auer von Welsbach independently isolated these elements from ytterbia at about the same time. Chemists eventually changed the name neoytterbium back to ytterbium, and similarly, the spelling of lutecium to lutetium. The chemical and physical properties of ytterbium could not be determined until 1953, when more purified samples of ytterbium sample were produced.

Lutetium (Lu; Z = 71): The name of this REE was originally ‘lutecium’ but in 1949, the IUPAC changed the ‘c’ to ‘t’ since the name derives from *Lutetia*, the ancient Latin name for the city of ‘Paris’, rather than from its French equivalent *lutece*. Three scientists independently found lutetium as an impurity in the mineral ‘ytterbia’. The discovery is credited to the French chemist Georges Urbain in 1907, although both Austrian chemist Carl Auer von Welsbach and American chemist Charles James declared similar findings. Auer von Welsbach named the element cassiopeium for the constellation ‘Cassiopeia’. Although a scientific paper written by Auer von Welsbach’s appeared prior to a similar discussion by Urbain, Urbain argued that he had submitted his paper to the editor first. The International Committee on Atomic Weights, where Urbain was one of the four members, adopted Urbain’s name and his claim of priority. The German Atomic Weights’ Committee accepted Auer von Welsbach’s name of cassiopeia for the element for the next forty years. Urbain’s name for the element was officially adopted by the IUPAC in 1949 based on consideration of prevailing usage, finally ending the controversy. Ironically, Charles James, who had avoided the public controversy, worked on a much larger scale than the others, and probably possessed the largest supply of lutetium at the time.

Table 1.3 and Figure 1.4 provide summaries of the eminent chemists responsible for the discovery and naming of the rare-earth elements.

Table 1.3. Chronological discovery record of the rare-earth elements.

Element (chemical symbol)	Atomic number	Year	Discoverer	Origin of name
Yttrium (Y)	39	1794	Johan Gadolin (Finnish)	Ytterby mine, Sweden
Cerium (Ce)	58	1803	Jöns Jacob Berzelius (Swedish); Wilhelm von Hisinger (Swedish); Martin Heinrich Klaproth (German)	Small planetoid Ceres
Lanthanum (La)	57	1839	Carl Gustaf Mosander (Swedish)	Greek: <i>lanthano</i> for 'to lie hidden or to escape notice' since it lay concealed in the earth
Terbium (Tb)	65	1843	Carl Gustaf Mosander (Swedish)	Ytterby mine, Sweden
Erbium (Er)	68	1843	Carl Gustaf Mosander (Swedish)	Ytterby mine, Sweden
Holmium (Ho)	67	1878	Jacques-Louis Soret (Swiss); Marc Delafontaine (Swiss); Per Theodor Cleve (Swedish)	Latin: <i>holmia</i> for 'Stockholm'
Ytterbium (Yb)	70	1878	Jean Charles Galissard de Marignac (French)	Ytterby mine, Sweden
Scandium (Sc)	21	1879	Lars Fredrik Nilson (Swedish)	Latin: <i>scandia</i> for 'Scandinavia'
Samarium (Sm)	62	1879	Paul Émile Lecoq de Boisbaudran (French)	The mineral samarskite and its finder, the Russian mine official Colonel von Samarsky
Thulium (Tm)	69	1879	Per Theodor Cleve (Swedish)	Latin: <i>Thule</i> for ancient name for 'Scandinavia'
Gadolinium (Gd)	64	1880	Jean Charles Galissard de Marignac (Swiss)	Hebrew: <i>gadol</i> for 'great' and in honour of Finnish chemist Johan Gadolin
Praseodymium (Pr)	59	1885	Carl Auer von Welsbach (Austrian)	Greek: <i>prasios</i> for 'green' in reference to the colour of its salts, and <i>didymos</i> for 'twin', because of its resemblance to another closely related REE, lanthanum
Neodymium (Nd)	60	1885	Carl Auer von Welsbach (Austrian)	Greek: <i>neos</i> for 'new-one' and <i>didymos</i> for 'twin'
Dysprosium (Dy)	66	1886	Paul Émile Lecoq de Boisbaudran (French)	Greek: <i>dysprositos</i> for 'hard to get at' because of the difficult involved with its detection and isolation
Europium (Eu)	63	1896	Eugène-Anatole Demarçay (French)	After the continent Europe, which itself comes from <i>Europa</i> in Greek mythology
Lutetium (Lu)	71	1907	Georges Urbain (French)	Latin: <i>Lutetia</i> for the place where Paris was founded
Promethium (Pm)	61	1945	Charles D. Coryell; Jacob A. Marinsky; Lawrence E. Glendenin (all American)	Greek: Prometheus who brought fire to mankind in reference to harnessing of the energy of the nuclear fission and warning against its dangers



Johan Gadolin
(1760–1852)
Finnish chemist



Martin Klaproth
(1743–1817)
German chemist



Carl Gustav Mosander
(1797–1858)
Swedish chemist



Per Theodor Cleve
(1840–1905)
Swedish chemist



Jean Charles Galissard de Marignac
(1817–1894)
Swiss chemist



Paul Émile Lecoq de Boisbaudran
(1838–1912)
French chemist



Dmitri Mendeleev
(1834–1907)
Russian chemist



Carl Auer von Welsbach
(1858–1929)
Austrian chemist

Figure 1.4. Famous European chemists responsible for the discovery and confirmation of the rare-earth elements (REE). Many of the REE identified during the eighteenth and nineteenth centuries were named in recognition of the scientist who found them or defined their elemental properties. Other elements were named after their geographical source location, or were derived from a Greek or Latin mythical heritage. All photographs are from Wikimedia Commons (http://commons.wikimedia.org/wiki/Main_Page).

1.3. MAJOR PROPERTIES AND APPLICATIONS

The REE have unique and diverse chemical, magnetic, and luminescent properties that make them strategically important in a number of high-technology industries. Traditionally they have been used for colouring and polishing glass, sintering aids in ceramics, car engine exhausts, magnets, catalysts, and metallic alloys in metallurgy. However, their applications in many emerging technologies associated with the transport, information, environment, energy, defence, nuclear, and aerospace industries have gained rapid momentum in recent years. The most significant increases in demand are the predicted expansion in hybrid car components (primarily batteries and magnets), compact fluorescent light bulbs, phosphors in computer and plasma screens, petroleum catalysts, superconductors, samarium-cobalt and neodymium-iron-boron high-flux supermagnets in electric motors for hybrid cars and wind turbine generators, glass manufacturing, electronic polishing, fuel-cell technology, and multi-level electronic components such as DVD drives. Oxides of the REE are now used in the environment as chemical tracers to monitor geological materials associated with river catchments and to determine erosion rates of drainage-watershed systems (Fig. 1.5).

Curtis (2011) has forecasted that the future demand for REE in most applications will increase with battery alloys and magnets being the most dominant growth drivers. For example, projected annual growth rates of REE are estimated for the following applications: battery alloys (15%); magnets (12%); polishing powder (10%);



Figure 1.5. Rare-earth oxides that are used as chemical tracers to determine which parts of a watershed are eroding. Clockwise from top centre: praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium. Reproduced with permission (PD-USGOV-USDA-ARS) from the United States Department of Agriculture, Agricultural Research Service, at <http://www.ars.usda.gov/is/graphics/photos/jun05/d115-1.htm> Group Elements (red font). Modified from Haxel et al. (2005).

autocatalysts (8%); phosphors (8%); fluid cracking catalysts (4%); metallurgy (2%); and others (8%).

The REE are also becoming increasingly more important in many defence-related applications (http://www.molycorp.com/defense_applications.asp). The REE are used in many forms from low-purity concentrates and natural mixtures of metal ('mischmetal') to ultra high-purity compounds and metals.

The smallest commercial sector by volume, but largest by value, is europium and terbium, which are used in the production of phosphors for television media and energy efficient light globes (Miezitis, 2010). In 1967, europium was the first, high purity REE to enter the public marketplace as a source of the red colour in television sets. There had been colour monitors before the use of europium, but the colour quality was generally weak. The early televisions relied on phosphors—substances that glow when struck with electrons or other energised particles—to get their red, green, and blue colours, and the early red phosphors could not produce a very bright colour. Europium phosphors dramatically improved the quality of television pictures. Figure 1.6 summarises the distribution of REO applications according to value and volume.

1.3.1. Properties and applications of individual rare-earth elements

Scandium: A silvery-white metallic transition metal, scandium has historically been sometimes classified as a REE, together with yttrium and the lanthanides. Metallic scandium was first produced in 1937 and the first pound (0.45 kilograms) of pure scandium was produced in 1960. Scandium is rarely concentrated in nature because of its lack of affinity to combine with the common ore-forming anions. Its abundance is thought to be about 5 to 6 parts per million (ppm) in the Earth's crust. Interestingly, scandium is more common in the sun and certain stars than on Earth. Scandium is present in most of the REE and uranium deposits, but it is extracted from these ores in only a few mines worldwide. Its use is severely restricted by its scarcity of reliable supply as there are no primary scandium mines in production in the world. Scandium is found in common rock-forming minerals, such as biotite, hornblende, and pyroxene, and in trace amounts (5 to 100 ppm) in basalt and gabbro. Scandium also occurs in aluminium phosphate minerals, beryl, cassiterite, columbite, garnet, muscovite, REE minerals, and wolframite. Scandium can also be obtained from the rare minerals thortveitite

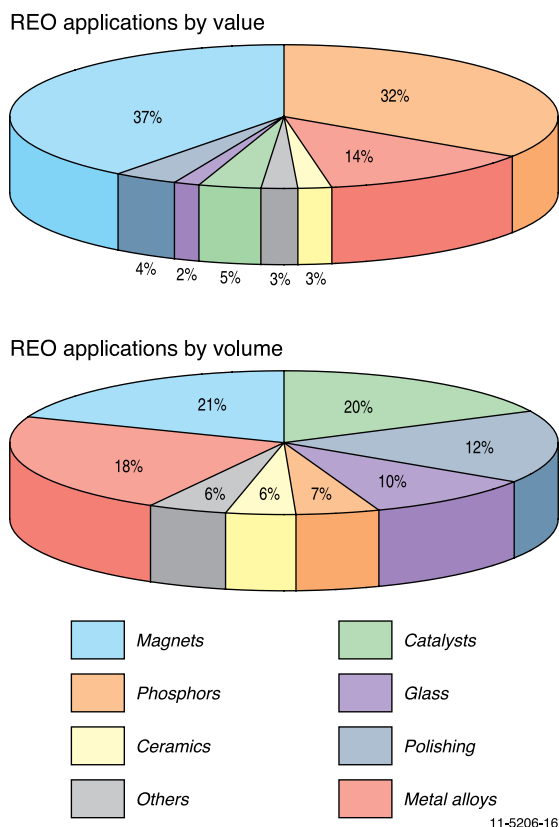


Figure 1.6. The major applications of the rare-earth oxides by value and volume. Modified from Kingsnorth (2010b).

$[(\text{Sc},\text{Y})_2\text{Si}_2\text{O}_7]$, which contains 44–48% scandium oxide Sc_2O_3 , bazzite ($\text{Be}_3(\text{Sc},\text{Al})_2\text{Si}_6\text{O}_{18}$), wiikite (ill-defined mixture of REE), euxenite, and gadolinite, but it is usually obtained as a by-product of refining uranium and tantalum. Most scandium not obtained from uranium tailings is mined from Iceland, Madagascar, and the Scandinavian Peninsula.

Being a soft and light metal, scandium has alloy applications with aluminum in the aerospace industry. These alloys contain between 0.1 to 0.5% of scandium and are amongst the lightest and strongest alloys in the world. Companies that use scandium often buy the oxide rather than the pure metal. The oxide costs several thousand dollars per kilogram. By comparison, the pure metal costs a few hundred thousand dollars per kilogram therefore scandium is too expensive for widespread use. Due to its low availability and the difficulties in the preparation of metallic scandium, it took until the 1970s before applications for scandium were developed. Scandium's industrial applications include its ability to improve strength, ductility, and other properties when added to aluminum. Alloys of scandium and aluminum are also used in sporting equipment, such as aluminum baseball bats, bicycle frames, and lacrosse sticks. Scandium-stabilised zirconia

as an electrolyte for Solid Oxide Fuel Cells (SOFC) significantly reduces the operating temperature of fuel cells, thereby providing a much longer life. SOFCs are expected to play a major role in the developing battery powered electric transportation industry. The enhanced application of SOFC has recently increased the global interest in scandium. Scientists have only studied a few compounds of scandium. About 20 kilograms (44 pounds) of scandium oxide (Sc_2O_3), also known as scandia, are used each year in the USA in the production of high-intensity discharge lamps, colour televisions, energy-saving lamps, glasses, and speciality welding wire. Scandium iodide (ScI_3) is added to mercury vapor lamps so that they will emit light that closely resembles sunlight. The radioactive isotope ^{46}Sc is used as a tracing agent in crude oil refinery crackers.

Yttrium: Yttrium is a soft, silver-metallic, lustrous and highly crystalline transition metal that generally forms inorganic compounds in the oxidation state of +3. It is chemically similar to the lanthanide elements, and it has traditionally been classified a REE. Yttrium is primarily obtained through an ion exchange process from monazite sand, a material rich in REE. It is a scarce metal that is also known as a blackish grey powder that never produces a spectrum.

Although metallic yttrium is not widely used, several of its compounds are currently utilised. Yttrium oxide (Y_2O_3) and yttrium orthovanadate (YVO_4) are both combined with europium to produce the red phosphor used in colour television picture tubes. Yttrium oxide is suitable for making superconductors, which are compounds that conduct electricity without any loss of energy. Yttrium metal is added to aluminium and magnesium to increase the strength of the alloy, and it is added to cast iron to enhance the workability of the metal. Metal alloys comprising yttrium, chromium, and aluminium are heat resistant and conduct heat. Yttrium oxide in glass and ceramics makes it heat- and shock-resistant, which has application in camera lenses. Garnets made from yttrium and iron ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) are used as microwave filters in microwave communications equipment, resonators in frequency meters, magnetic field measurement devices, tunable transistors, and oscillators. Garnets made from yttrium and aluminum ($\text{Y}_3\text{Al}_5\text{O}_{12}$) are used in jewellery as simulated diamond. Yttrium is also used in the manufacturing of gas mantles for propane lanterns as a replacement for thorium, which is radioactive. Yttrium-based materials improve the efficiency of car engines and high-performance spark plugs. Radioactive isotopes of yttrium have medical applications for the treatment of cancers, nerve problems in the spinal chord, and rheumatoid arthritis.

Lanthanum: Lanthanum is a shiny grey, ductile, graphitic-like metal, and a dark lead-grey powder, soft to touch, and able to be pressed into a compact mass. It is found in some rare-earth minerals, usually in combination with cerium and other REE. Lanthanum is the first element of the lanthanide series, exhibits two oxidation states, +3 and +2, the former being much more stable, and it rapidly oxidises in air.

Important applications for lanthanum were not found for over one hundred years. The initial interest for lanthanum was largely scientific, being limited to investigators improving its separation techniques, purification, and defining its chemical spectrum. The first historical application of lanthanum was patented in 1885 for its use in gas lantern mantles. Its activity in catalysts for petroleum refining increases refinery yield by up to 10% while reducing overall power consumption. As most hybrid cars use nickel-metal hydride batteries, significant quantities of lanthanum are required for the production of hybrid automobiles. Typical hybrid automobile batteries require about 10 to 15 kg of lanthanum. Lanthanum is used to make carbon arc lights that are utilised in the motion picture industry for studio lighting and projector lights. Various compounds of lanthanum and other REE (oxides, chlorides, etc.) are components of various catalysis, such as petroleum cracking catalysts. Lanthanum also makes up about 25% of 'misch' metal, a material that is used to make flints for lighters. Lanthanum-bearing hydrogen sponge alloys are capable of storing up to 400 times their own volume of hydrogen gas in a reversible adsorption process. Lanthanum oxides (La_2O_3) improve the alkali resistance of glass, and are used in making special optical glasses (e.g., infrared-absorbing glass) and camera and telescope lenses because of the high refractive index and low dispersion of rare-earth glasses.

Cerium: Cerium is a soft, malleable, ductile, and shiny grey metal that readily oxidises to a green oxide, and reacts quickly in hot water. Pure cerium will ignite if it is scratched with a sharp object, but can be safely used if combined with other materials. The most common oxidation states are +3 and +4, followed by +8. Cerium is the most abundant of the REE with about 60 ppm occurring in the Earth's crust (Table 1.1). Important Ce-bearing minerals (Table 1.2) include allanite or orthite, rhabdophane, and synchysite, and its major sources are bastnäsite, hydroxylbastnäsite, and monazite.

Cerium is critical in the manufacture of environmental protection and pollution-control systems, from cars to refineries. It is used as a catalyst to refine petroleum and to oxidise unreacted hydrocarbons and reduce nitrogen

oxides. As a diesel fuel additive for micro-filtration of pollutants, it promotes more complete fuel combustion for more energy efficiency. Cerium is used in carbon arc lights for studio lighting and projector lights, and is a component of 'misch' metal for flints in lighters and as an alloying agent to make special metals in permanent magnets and in tungsten electrodes for gas tungsten arc welding. Cerium oxide (Ce_2O_3 and CeO_2) is a component of the walls of self cleaning ovens and of incandescent lantern mantles. Cerium oxide (CeO_2) is used as an abrasive to polish glass surfaces in lenses and CRT displays, and to extend the life of the glass and improve its colour dispersion. Cerium sulphide (Ce_2S_3) in red pigments is increasingly being used in place of toxic cadmium salts. Ceric sulphate ($\text{Ce}(\text{SO}_4)_2$) has applications in some chemical analysis processes. Other cerium compounds are used to make some types of glass as well as to remove colour from glass.

Praseodymium: Praseodymium is a soft, malleable, ductile, and reflective grey metal that reacts slowly in air to develop a green oxide coating, but it is very reactive in water. Its most common oxidation state is +3. Praseodymium is primarily sourced from bastnäsite and monazite.

The primary use of praseodymium is as an alloying agent with magnesium to create high-strength metals that are used in aircraft engines and in permanent magnet (neodymium-iron-boron) systems of small motors. It also makes up about 5% of 'misch' metal used in the making of flints for lighters. Praseodymium forms the core of high-intensity carbon arc lights used in the motion picture industry for studio lighting, projector lights, floodlights, and searchlights. Along with neodymium, it can filter certain wavelengths of light, such as in photographic filters, airport signal lenses, and tinted enamels and glass. For example, it forms a component of yellow didymium glass used in welder's and glass blower's goggles for protection against infrared radiation. Praseodymium is added to fiber optic cables as a doping agent where it is used as a signal amplifier. Praseodymium alloyed with nickel (PrNi_3) has such a strong magnetocaloric effect that it has allowed scientists to approach within one thousandth of a degree of absolute zero temperature.

Neodymium: Neodymium is a soft, malleable, ductile, reflective grey metal that easily oxidises in both air and water, and it is found in the +3, +2, and +4 oxidation states. Neodymium is not found naturally in metallic form or unaccompanied by other lanthanides. It is present in significant quantities in the ore minerals monazite and bastnäsite.

Neodymium compounds were first commercially used as a glass dye in 1927. Neodymium is an important component of metal alloys. When alloyed with iron and boron, it forms extremely strong permanent magnets (called rare-earth magnets or neodymium magnets), and it is used to strengthen alloys of magnesium. Cell phones, microphones, CD players, computer hard disks, and most sound systems use neodymium magnets. Neodymium-Iron-Boron (NdFeB) magnets maximise the power/cost ratios of various motors and mechanical systems. Neodymium makes up about 18% of 'misch' metal that is used to make flints for lighters. Neodymium is also a component of didymium glass, which is used to make certain types of welder's and glass blower's goggles. Neodymium is added to glass to remove the green colour caused by iron contaminants. It can also be added to glass to create violet, red, or grey colours. Some types of glass containing neodymium are used by astronomers to calibrate spectrometers and other types are used to create artificial rubies for lasers. Some neodymium salts are used to colour enamels and glazes.

Promethium: Promethium does not occur naturally on Earth, although it has been detected in the spectrum of a star in the constellation Andromeda. Promethium is an unstable radioactive element only found in trace amounts in uranium ores and recovered from the byproducts of uranium fission. Due to its instability, promethium does not accumulate above the concentration of about a picogram (10^{-12}) per tonne of ore. Promethium's most stable isotope, ^{145}Pm , has a half-life of 17.7 years. It decays into Nd^{145} through electron capture.

Promethium could be used to make a nuclear powered battery. This type of battery would use the beta particles emitted by the decay of promethium to make a phosphor give off light. This light would then be converted into electricity by a device similar to a solar cell. It is expected that this type of battery could provide power for five years. Due to its instability, promethium has few practical applications. Minor uses include beta radioactive sources for gauges that measure the thickness of sheets of steel and luminous blue and green paints on the face of watches. Potential applications include: portable X-ray sources in radioisotope thermoelectric generators that provide heat or power for space probes and satellites; miniature batteries in missiles and pacemakers; and in lasers that communicate with submerged submarines.

Samarium: Samarium is a high lustre, silvery, moderately hard metal obtained from monazite (which contains up to 2.8% samarium), bastnäsite,

gadolinite, and samarskite. Stable in dry air, samarium oxidises in moist air and ignites when heated to 150°C . Within its compounds, it usually displays +2 and +3 oxidation states.

Samarium is used in carbon-arc lights for the motion picture industry, studio lighting, and projector lights. Its spectral absorption properties make it useful in filter glasses that surround neodymium laser rods and as a neutron absorber in nuclear reactors. It makes up about 1% of 'misch' metal, a material used in the manufacture of flints for lighters. Samarium forms a compound with cobalt (SmCo_5) in powerful permanent magnets that have the highest resistance to demagnetisation of any material known, and they can withstand high temperatures, above 700°C , without losing magnetic properties. These magnets are used in headphones, small motors, magnetic pickups for guitars, and in solar-powered aircraft. Radioactive samarium isotopes (^{153}Sm) kill cancer cells in the treatment of lung, prostate, and breast cancer. Samarium oxide (Sm_2O_3) is added to glass to absorb infrared radiation and acts as a catalyst for the dehydration and dehydrogenation of ethanol ($\text{C}_2\text{H}_6\text{O}$). Other applications include catalysis of chemical reactions, radioactive dating, and an X-ray laser.

Europium: Europium is a moderately hard, silvery-grey metal that is the most reactive of the REE. It readily oxidises in air and water, and ignites when heated to 180°C . The dominant oxidation states of +2 and +3 are the same as samarium. Europium is never found in nature as a free element, however, it is hosted by many minerals, including monazite and bastnäsite.

There are no major commercial applications for europium metal, although it has been used to dope some types of plastics to make lasers. Europium has exceptional properties relating to photo emission. When it absorbs electrons or UV radiation, the europium atom changes energy levels to create a visible luminescent emission. Europium oxide (Eu_2O_3) is widely used as a red phosphor in the cathode-ray tubes of television sets and computer monitors, and as an activator for yttrium-based phosphors. Since it is a good absorber of neutrons, europium is being investigated for use in nuclear reactors. Europium has also been identified in the spectra of the sun and certain stars. Europium is added to fluorescent lighting to enhance a blue component for a more natural light, and to reduce up to 75% of the energy costs compared to incandescent lighting. Europium fluorescence is used to interrogate biomolecular interactions in drug-discovery screens, and in the anti-counterfeiting phosphors in Euro banknotes. Medical applications include tagging

complex biochemical agents for tracing materials during tissue research, and the screening of genetic diseases, such as Down's Syndrome. Geoscientists use depletion or enrichment concentrations of europium (called the europium anomaly) in minerals and rocks to understand geological processes.

Gadolinium: Gadolinium is a soft, ductile, silvery-white metal that is relatively stable in dry air, but oxidises in moist air and dissolves in water and acid. In the great majority of its compounds, gadolinium usually adopts the +3 oxidation state. The minerals monazite and bastnäsite are the primary sources.

Gadolinium has no large-scale applications, but it has a variety of specialised uses. It can be alloyed with iron, chromium, and other metals to improve their workability and their resistance to high temperatures and oxidation. With its unique magnetic behaviour, it is used in magnets for such electronic devices as disk drives, video recorders, compact disks, and in handling computer data and magneto-optic recording. Gadolinium can be combined with yttrium to form garnets that have applications in microwave technology, and gadolinium compounds are used to make green phosphors for colour televisions and compact disks. Gadolinium has the highest neutron cross-section of any stable nuclide and the greatest ability to capture thermal neutrons of all known elements. It is therefore used for shielding devices in neutron radiography, in magnetic resonance imaging for the detection of cancers, X-ray systems, and in control rods in nuclear reactors. Unfortunately, the two isotopes best suited for neutron capture, gadolinium-155 and gadolinium-157, are present in small amounts. As a result, gadolinium-based control rods quickly lose their effectiveness.

Terbium: Terbium is a soft, silvery-white metal that is not found in nature as a free element. Terbium occurs in the minerals cerite ($\text{Ce}_9^{3+}\text{Fe}^{3+}(\text{SiO}_4)_6[\text{SiO}_3(\text{OH})](\text{OH})_3$), xenotime (YPO_4), and euxenite, but is primarily obtained from monazite that typically contains up to 0.03% terbium. It oxidises very slowly in air, dissolves in water, and as typical of most other REE, it adopts the +3 oxidation state. As with its neighbour element dysprosium, it is very soft and can be cut by a knife.

Terbium is used in some types of solid-state devices and, along with zirconium dioxide (ZrO_2), as a crystal stabiliser that operate at high temperatures in fuel cells. Terbium has applications in magnetorestrictive alloys, which lengthen or shorten when exposed to a magnetic field. Terbium oxide is used as an activator for green phosphors (which fluoresce a brilliant lemon-yellow)

in cathode-ray television tubes and energy-efficient fluorescent lamps. Terbium is also used in naval sonar systems, sensors, in the SoundBug device (its first commercial application), and other magnetomechanical devices. Terbium borate is used to make laser light.

Dysprosium: There are no major commercial applications for dysprosium, which is a silver, high-lustred metal that is so soft it can be cut with a knife. Dysprosium is not found in nature as a free element, and it is mainly obtained from monazite, xenotime, and bastnäsite. It is moderately reactive, oxidises in air, quickly dissolves in cold water, and has the dominant +3 oxidation state typical of the other REE.

Since it easily absorbs neutrons and has a high-melting point, dysprosium is alloyed with steel for use in nuclear reactors and in dosimeters for measuring exposure to radiation. When combined with vanadium and other REE, dysprosium is used in laser materials. Dysprosium oxide (Dy_2O_3) is combined with nickel and added to a special cement for cooling nuclear reactor rods. Its high magnetic susceptibility to magnetisation character is exploited in the manufacture of permanent magnets and data storage devices. Dysprosium has applications in high-precision liquid fuel injectors, transducers, wide-band mechanical resonators, and dysprosium iodide (DyI_3) is used in halogen lamps to enhance white light.

Holmium: Holmium is a soft, malleable, silvery-white metal that is stable in dry air at room temperature, but dissolves in acids. In its compounds, it is usually found in the +3 oxidation state. Some of holmium's compounds include holmium oxide (Ho_2O_3), holmium fluoride (HoF_3), and holmium iodide (HoI_3). It is primarily obtained from monazite, which can contain as much as 0.05% holmium.

Holmium is rare, expensive, and has no major commercial applications. Holmium has the highest magnetic strength of any element, and therefore is used to create the strongest artificially generated magnetic fields, when placed within high-strength magnets as a magnetic flux concentrator. Holmium is used in nuclear control rods where it has the ability to absorb nuclear fission-expelled neutrons. Holmium is an important REE component of microwave and laser equipment where the safety of human eyes is an issue during medical, dental, and fibre-optical procedures. Holmium also provides yellow and red colouring pigments for cubic zirconia and glass, and is used in calibration standards for optical spectrophotometers and gamma-ray spectrometers.

Erbium: Erbium is a soft, malleable, and grey-white metal that is stable in air, and does not oxidise as quickly as some of the other REE. It is largely obtained from the minerals xenotime, euxenite, monazite, and bastnäsite through an ion exchange process.

Erbium's everyday uses are varied. Erbium's principal uses involve its pink-colored Er^{3+} ions, which have optical fluorescent properties particularly useful in certain laser applications. The distinctive pink colour of erbium oxide is used to colour glass, cubic zirconia, porcelain, and glazes. Some of these tinted products are utilised in sunglasses and cheap jewellery. Erbium is commonly used as a photographic filter, and because of its resilience it is useful as a metallurgical additive. It can be alloyed with vanadium to make it softer and easier to shape. Erbium has remarkable optical properties and it is added to long-range fiber optic cables as a doping agent where it is used as a signal amplifier. High-power erbium–ytterbium fiber lasers are gradually replacing CO_2 lasers for metal welding and cutting applications. Erbium also has some uses as neutron-absorbing control rods in the nuclear power industry. Medical applications include dermatology, dentistry, and laser surgery. The erbium–nickel alloy Er_3Ni has an unusually high specific heat capacity at liquid-helium temperatures that is utilised in cryocoolers.

Thulium: Thulium is the least abundant of the naturally occurring REE. It is a soft and malleable, silvery grey metal that has only recently become available. Thulium is primarily obtained from monazite, which contains as much as 0.002% thulium, and bastnäsite, which contains as much as 0.0008% thulium. Thulium tarnishes in air very slowly, and it usually adopts the +3 oxidation state in its compounds. Its chemistry is similar to that of yttrium.

Rare and expensive, thulium has no major commercial applications. However, because of its unique photographic properties it is used in sensitive X-ray phosphors to reduce X-ray exposure, and one of its isotopes, ^{169}Tm , is used as a radiation source for portable X-ray machines. Such radiation sources have applications in medical and dental diagnosis, as well as detecting defects in mechanical and electronic components. Highly efficient thulium-based lasers are used in the military, medicine, meteorology, and surgery. Superficial ablation of skin tissue is carried out with thulium lasers that operate at wavelengths between 1930 and 2040 nm. As with yttrium, thulium is a REE component of high-temperature superconductors.

Ytterbium: Ytterbium is a malleable, ductile, and silvery metal that has few applications. It can be obtained from monazite, which has about 0.1% ytterbium, and from bastnäsite, which contains about 0.0006% ytterbium. Ytterbium oxidises slowly in air, but unlike other transition metals, the oxide does not flake off the surface, but forms a protective layer that inhibits further oxidation. It has similar chemical behaviour to yttrium, and as with most other REE, the dominant oxidation state is +3.

Ytterbium is alloyed with stainless steel to improve the strength and mechanical properties of dental tools, and it is also used as a doping agent in fiber optic cables for enhancement of amplification attributes. One of ytterbium's isotopes (^{169}Yb) is used as a radiation source substitute for portable X-ray machines. Such machines are useful for the radiography of small objects and when electricity is not available. Ytterbium is often used as a doping material (as Yb_3^+) for high power and wavelength-tunable solid-state lasers. When subject to high stresses, the electrical resistance of ytterbium increases by an order of magnitude. Subsequently it is used in stress gauges to monitor ground movements and deformations initiated by earthquakes and underground explosions.

Lutetium: Lutetium is a silvery-white, hard, dense metal that is one of the most difficult elements to prepare. With thulium, lutetium is the least abundant of the naturally occurring REE, and because of the difficulty of separating it from other elements, it is very expensive—much more expensive than gold and platinum. It is obtained from monazite, which contains about 0.003% lutetium. In contrast to the other REE, it is resistant to oxidation in air, but it has the common oxidation state of +3.

Lutetium is an expensive and rare metal that has no large-scale commercial uses. It often occurs in association with yttrium and is sometimes used in metal alloys and as a catalyst in various chemical reactions. Some radioactive isotopes of lutetium are used as a catalyst in the cracking of petroleum products, in some hydrogenation and polymerisation processes, and in detectors for positron emission tomography. The radioactive isotope lutetium-177 (^{177}Lu) is used experimentally in targeted radionuclide therapy for tumors, and lutetium-176 (^{176}Lu) is used in nuclear technology to determine the age of meteorites.

Table 1.4 summarises the major applications of the REE that are gaining momentum in high-technical industries, and many of these applications are shown in Figures 1.6 and 1.7.

Table 1.4. Major applications of the rare-earth elements in emerging high-technology industries.

Heavy-rare-earth elements are shown in <i>italic font</i> ; light-rare-earth elements are shown in normal font
(1) Catalysts: La, Ce, Nd, Pr, <i>Lu</i>, Y, Sm Automotive catalysts Petroleum refining, fuel catalytic cracking, ethane polymerisation Fuel and hybrids, diesel fuel additive Air pollution controls, water filtration, hydrogen storage, flints
(2) Permanent and ceramic magnets: Nd, Pr, Sm, <i>Dy</i>, <i>Tb</i>, <i>Tm</i>, La, Ce Cars—hybrids-plug-in and electric vehicles, window motors, screen wipers, starter motors, hybrid batteries, alternators, brakes Electronics—computer disc drives, data storage, iPods, DVDs, CDs, video recorders, consoles, video cameras, mobile phones Speakers, headphones, microphones, ceramic capacitors Wind-, hydro-, and tidal-power turbines Electrical motors, refrigeration, generators, cordless power tools Medical imaging Handheld wireless devices
(3) Phosphors: Y, Eu, <i>Tb</i>, <i>Gd</i>, Ce, La, <i>Dy</i>, Pr, Sc LCD televisions and monitors, plasma televisions and displays, mobile phone displays Energy efficient fluorescent lights, high-intensity lighting, LEDs, mercury-vapour lamps Phosphors—red (Eu), blue (Eu), and green (Tb)
(4) Polishing powders: Ce, La, Pr Television and computer screens—plasma, CRT Precision optical lenses and electronic components Silica wafers and chips, catalyst for self-cleaning ovens
(5) Glass additives: Ce, <i>Er</i>, <i>Gd</i>, <i>Tb</i>, La, Nd, Yb, Pm CRT screens to stabilise glass from cathode ray Glass—optical lenses, glass for digital cameras, tinted glass, UV-resistant glass, high-refractive index glass, fibre optics
(6) Ceramics: <i>Dy</i>, <i>Er</i>, Ce, Pr, Nd, <i>Gd</i>, <i>Ho</i>, La Colours in ceramics and glass —yellow (Ce), green (Pr), and violet (Nd)
(7) Energy storage: La, Ce, Pr, Nd, Pm Rechargeable NiMH batteries, battery electrodes, nuclear batteries
(8) Medical equipment: various REE MRI machines, X-ray imaging Surgical drills and tools, surgical lasers Electron beam tubes, computed tomography, neutron capture
(9) Other applications: Lasers—<i>Yb</i>, Y, <i>Dy</i>, <i>Tb</i>, Eu, Sm, Nd, Pr, <i>Gd</i>, <i>Ho</i>, <i>Er</i> Superconductors—<i>Gd</i>, Y Nuclear—Ce, <i>Er</i> Fertilisers—various REE High-technology alloys—<i>Yb</i>, Lu, <i>Er</i>, <i>Tb</i>, <i>Gd</i>, Eu, Sm, Nd, Pr, <i>Ho</i>, Sc

Ce = cerium, Dy = dysprosium, Er = erbium, Eu = europium, Gd = gadolinium, Ho = holmium, La = lanthanum, Lu = lutetium, Nd = neodymium, Pm = promethium, Pr = praseodymium, Sc = scandium, Sm = samarium, Tb = terbium, Tm = thulium, Y = yttrium, Yb = ytterbium.

Figure 1.7 (see opposite). Rare-earth elements are critical for many emerging technologies in a wide range of industries. Some of the major industries include: automobile, petroleum, glass, electronics, energy, solar, metallurgy, medical, space, defence, and entertainment.



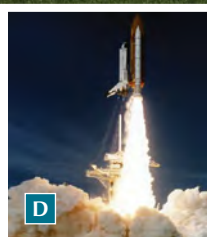
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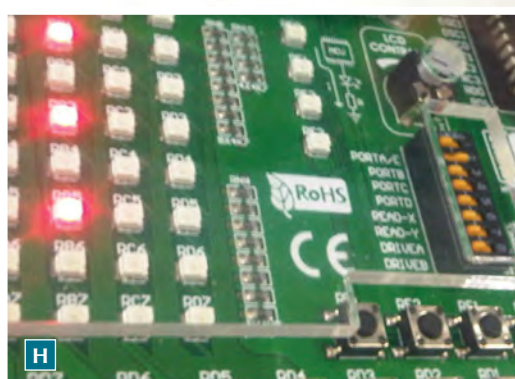
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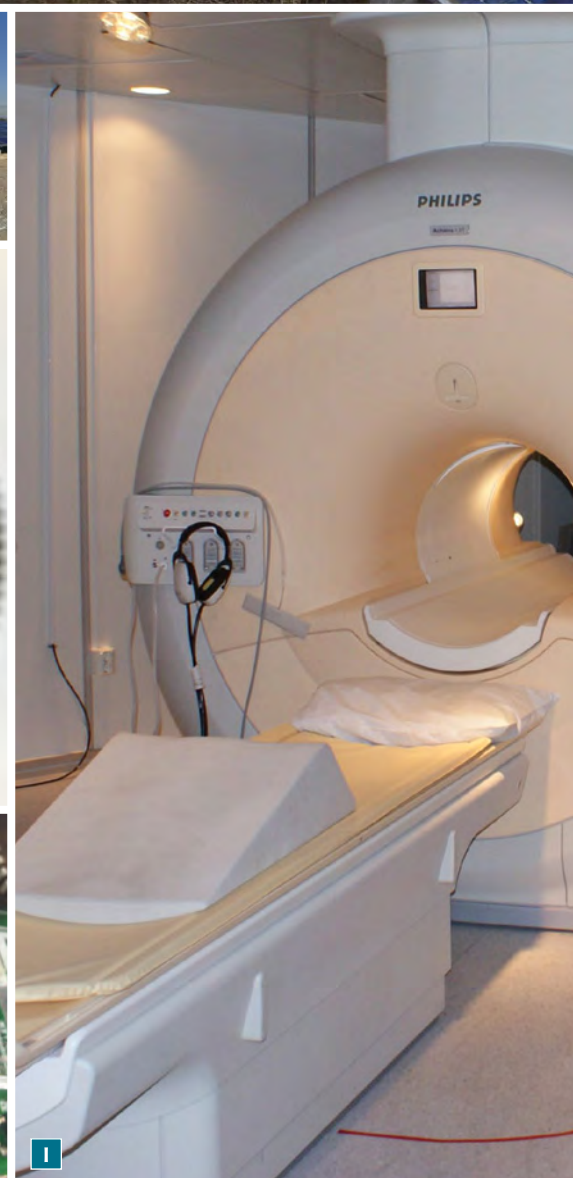
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1.4. GLOBAL PRODUCTION AND RESOURCES

For thousands of years, the mining of metals has been an integral part of man's social and economic development. Mining was the second of man's major endeavours, agriculture being the first (Kennedy, 1990). Such metals as gold, silver, PGEs, nickel, copper, lead, zinc, iron, manganese, and cobalt were mined in Medieval Europe (~14th century), during ancient Roman (early AD) and Egyptian (~2500 BC) times, and there are examples of iron being used some 43 000 years ago during Prehistoric times (e.g., hematite was ground to red pigment ochres at the 'Lion Cave' in Swaziland: http://en.wikipedia.org/wiki/Mining#Prehistoric_mining). Metals during the earliest phases of man's evolution were mainly used for decoration rather than for utility purposes because of their unique characteristics and rarity.

The commercial significance of the REE was not fully realised until the twentieth century with their global production gaining rapid momentum after the mid-1960s. The late evolution of the REE relative to other metals is attributed to the difficulty of isolating such metals with similar atomic structures and chemical properties, and separation analytical techniques that were critical to the accurate identification of the REE were only developed after the 1950s.

The mining of significant amounts of REE began in 1880 (Fig. 1.8). The REE were derived from monazite

for the manufacture of incandescent mantles for the Welsbach gas light. Most of this period's production came from monazite in extensive beach sand deposits in Brazil, and from India when it entered the world market in 1911. Minor amounts of REE were also obtained from monazite-bearing alluvial placer deposits in Sri Lanka, and North America (Idaho and Carolina monazite belt), and later from Malaysia, Thailand, and Australia (described in Section 1.5). Both Brazil and India dominated the world REE market until the 1940s. Most of these deposits contained a high LREE component and were prone to high levels of radioactivity. Production from these small alluvial sources scaled down during the 1950s to 1960s (Fig. 1.8) at a similar time to when new 'hard-rock' sources of these elements were being found to be hosted with a number of minerals, including monazite, bastnäsite, and xenotime, and with ion-adsorption clays (Steinitz, 2010). Modest amounts of REE were produced from monazite veins, pegmatites, and carbonatite intrusions, and as by-products of uranium and niobium deposits. During the 1950s, REE-bearing veins in South Africa were an important source of REE, and China began recovering minor REE as a by-product of iron and steel production in Mongolia. In 1953, global demand of REO totalled just 1000 tonnes valued at \$25 million compared to 2.7 million tonnes of copper worth \$1.7 billion for that year. In the mid-1960s, the global production of REE changed dramatically with the introduction of the Mountain Pass deposit in the upper Mojave Desert of California. Discovered in 1949 and commencing production in 1952, the

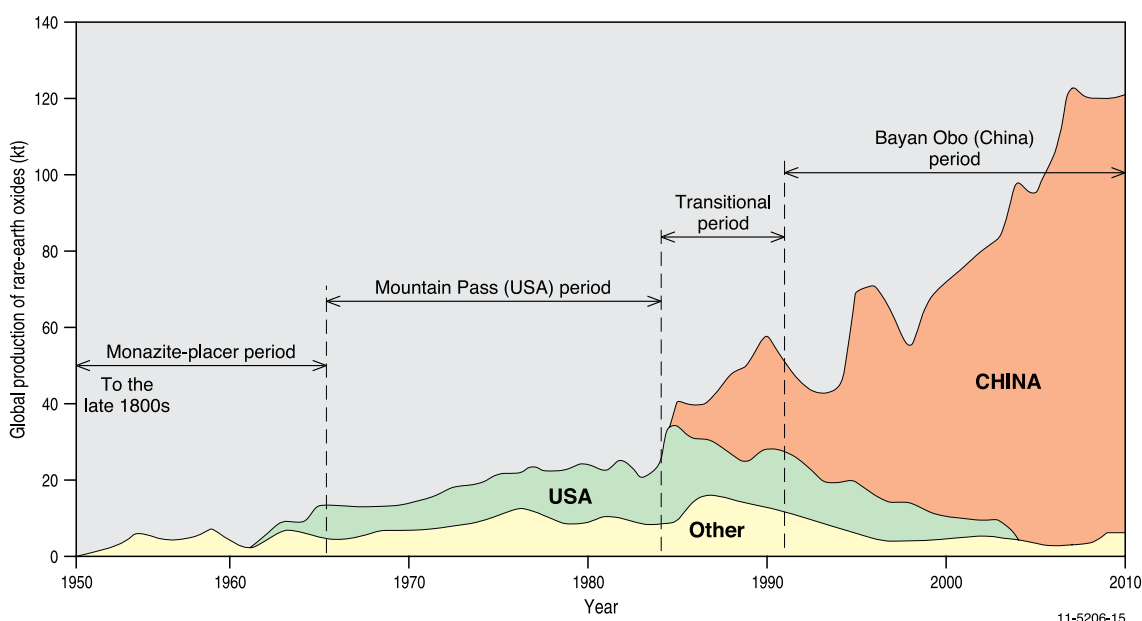


Figure 1.8. Global production of rare-earth oxides, 1950 to 2010. The relative minor production contribution from other countries is largely from monazite-bearing placers. Modified from Haxel et al. (2005).

world-class Mountain Pass deposit contains high concentrations of REE (8 to 12% REO) in a large carbonatite intrusion. The deposit is characterised by high levels of LREE along with much lower levels of radioactivity than the placer deposits. The carbonatite is a moderately dipping, tabular 1400 million years intrusive body associated with ultrapotassic alkaline plutons of similar age (Castor, 2008). From the mid-1960s to the 1990s, Mountain Pass was the world's largest source of REE. In the mid-1980s, it produced one third of the global supply of REO and 100% of the USA demand. Peak output was 20 000 tonnes of REO in 1990. Early development of the deposit was fast-tracked by the sudden demand for europium created by the commercialisation of colour televisions. By 1990, fourteen countries were mining REE with the USA the largest producer due to the contributions of the Mountain Pass deposit (Steinitz, 2010). During this period the USA was largely self sufficient in REE, but the USA soon became dependent on imports from other countries, and in particular China. After 1998,

Mountain Pass REE sales declined substantially due to competition from China and to environmental constraints. Mountain Pass ceased mining in 2002. From 2000 onwards, more than 90% of REE required by the USA came from deposits in China. As of 2010, the Mountain Pass deposit had proven and probable reserves of 13 588 000 tonnes of 8.24% TREO, equating to 1 120 000 tonnes of contained metals. The Mountain Pass deposit is planned to resume production by 2012 (Long et al., 2010).

China's contribution to the global scene commenced in the mid-1980s when it actively supported research and development into the REE and it became a producer on the world stage. The industry initially grew rapidly in an unregulated fashion spawning businesses of all sizes from huge state-owned enterprises, through small businesses running REE processing plants to artisanal miners. By 1992, it had become the world's largest producer of LREE and HREE (Fig. 1.9; Appendices 3 and 4). The REE are mined very cheaply in China,

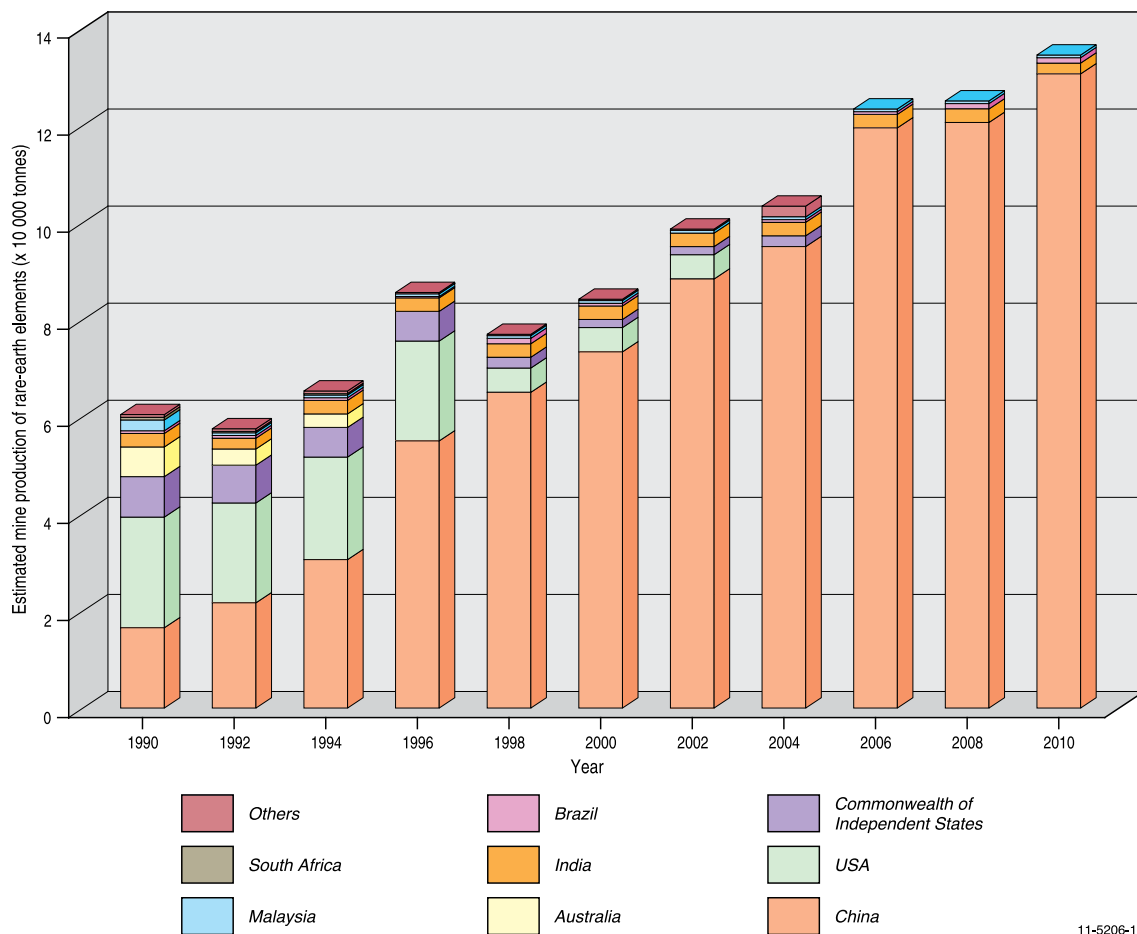


Figure 1.9. Estimated mine production of rare-earth elements for the major producing countries. Data from the United States Geological Survey Mineral Commodity Summaries, 1990 to 2011: Rare Earths (http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/). Others = other countries, including Madagascar, Sri Lanka, Thailand, Congo (Kinshasa), and Zaire.

either as a by-product of iron production at Bayan Obo, Inner Mongolia, or from lateritic REE-rich clays in southern China. The Bayan Obo iron-niobium-REE deposit (Drew et al., 1990; Fan et al., 2004) is the largest REE deposit in the world, as well as being a major producer of niobium and iron. It has geological similarities with both carbonatite REE deposits and to hydrothermal Cu-Au-U-REE iron-oxide deposits, such as Olympic Dam in South Australia and Kiruna in Sweden. Bayan Obo contains hydrothermal REE-enriched iron ores that have bastnäsite [(Ce, La, Y) CO₃F] and monazite as the main REE-bearing minerals. Resources at Bayan Obo total at least 48 million tonnes REO + Inferred + Subeconomic Resources) at grades of 3 to 6% REO. Another source of REE in China is ion-adsorption ores associated with lateritic clays developed on granitic and syenitic rocks in tropical southern China. Haxel et al. (2005) noted that these ores have the advantages of being enriched in the more valuable HREE and the metals are relatively easy to mine and extract. These deposits are currently the major supplier of these metals, as well as the focus of environmental controversy in China. By 2000, China accounted for 88% of world production, and some nine years later this has grown to 95.5%. Chinese leader Deng Xiaoping, recognised the strategic importance of these resources when he declared, “There is oil in the Middle East; there is rare earth in China” (Steinitz, 2010).

Global production trends of REE from 1950 to 2010 are summarised in Figure 1.8. Haxel et al. (2005) recognised four major global production periods, namely: a monazite-placer period starting in the late 1800s through to the mid-1960s; the Mountain Pass (USA) period commencing in 1965 and ending around 1984; a transitional period of mixed contributions from China, USA, and other countries from 1984 to 1991; and the Bayan Obo (China) period starting in 1991 and which continues to increase production to the present day. This figure clearly highlights the recent global dominance of China’s impact at the expense of REE production from other countries including, most notably, the USA.

As mentioned above, China dominates the global REE scene, accounting for about 95% (129 000 tonnes TREO: Table 1.5; Figure 1.9) of total production in 2009, while both India and the Commonwealth of Independent States (former members of the Soviet Union) contributed about 2%. In 2010, China holds 55 million tonnes (48.3%) of the world’s economic reserves of TREO, followed by the Commonwealth of Independent States with 19 million tonnes (16.7%) and the USA with 13 million tonnes (11.4%). Australia’s global REE impact in 2009 was negligible, with no recorded production and total Economic Demonstrated Resources (EDR) in 2010 amounting to 1.65 million tonnes of REO (1.45%).

Table 1.5. World production (2009) and resources (2010) of rare-earth oxides (modified from Cordier, 2011).

	Production (2009)		Resources (2010)	
	TREO (tonnes)	Share (%) Excluding other countries	TREO (tonnes)	Share (%)
Australia ¹	0	0	1 650 000	1.45
Brazil	550	0.41	48 000	0.04
China	129 000	95.48	55 000 000	48.32
Commonwealth of Independent States ²	2500	1.85	19 000 000	16.69
India	2700	2.00	3 100 000	2.72
Malaysia	350	0.26	30 000	0.03
United States of America	0	0	13 000 000	11.42
Other countries ³	NA	NA	22 000 000	19.33
Total	135 100	100	113 828 000	100

¹ Economic Demonstrated Resources for Australia as estimated by Geoscience Australia.

² Production for Commonwealth of Independent States (former members of the Soviet Union) from Long et al. (2010).

³ Other countries include South Africa, Sri Lanka, and Thailand.

NA = Not Available.

Figure 1.10 shows the relationships between the global supply (histograms) and demand (green graph) of REE for the period 1992 to 2010. Predicted trends are also shown up to 2014. In general, there has been a fairly consistent increase for both supply and demand for the REO until they experienced a significant decline during the global financial crisis, falling by a third in 2009. However, demand has since rebounded and the number of applications continues to soar. Current demand for REE is forecast to maintain a strong growth from the current level of around 124 000 tonnes per annum (tpa) REO, which has an estimated value of US\$1.5 billion, to about 175 000 tpa in 2014 (Kingsnorth, 2010a). This forecasted rapid increase in demand is shown by the dashed green line in Figure 1.10. The most significant increases in demand are predicted for hybrid cars, followed by petroleum catalyst, glass manufacturing and polishing, and multi-level electronic components. Expansion in new potential technologies include tidal power generation turbines, hydro power generation, magnetic refrigeration, and eBikes (Steinitz, 2010). The main global consumers of REE are China, USA, Japan, Korea, and Thailand with China reportedly accounting for about 60% of the world's consumption.

The central Chinese government has recently imposed production and export restrictions, adding upward pressure on prices for REE and contributing to incentives for development of REE resources outside China. Galaxy Resources Limited reported (http://www.galaxyresources.com.au/documents/DocGXY-151GalaxyCompletesReviewofPontonRareEarthsProject110111_000.pdf) in late 2010, that the Chinese Ministry of Commerce announced a 35% reduction in the export quota for the first half of 2011, compared to the corresponding period in 2010. This coincided with the launch of a nationwide crackdown on illegal mining of REE in China. The Chinese Government has also encouraged large companies to consolidate the country's REE inventory to prevent the resource from being undervalued. With China's moves to reduce export quotas, and stricter controls on illegal mining, several of the REE (e.g., neodymium) significantly increased in price. Consequently, over 200 REE mining projects throughout the world are being closely assessed, and in many cases re-examined, for potential mining operations, including the Mountain Pass REE deposit in the United States.

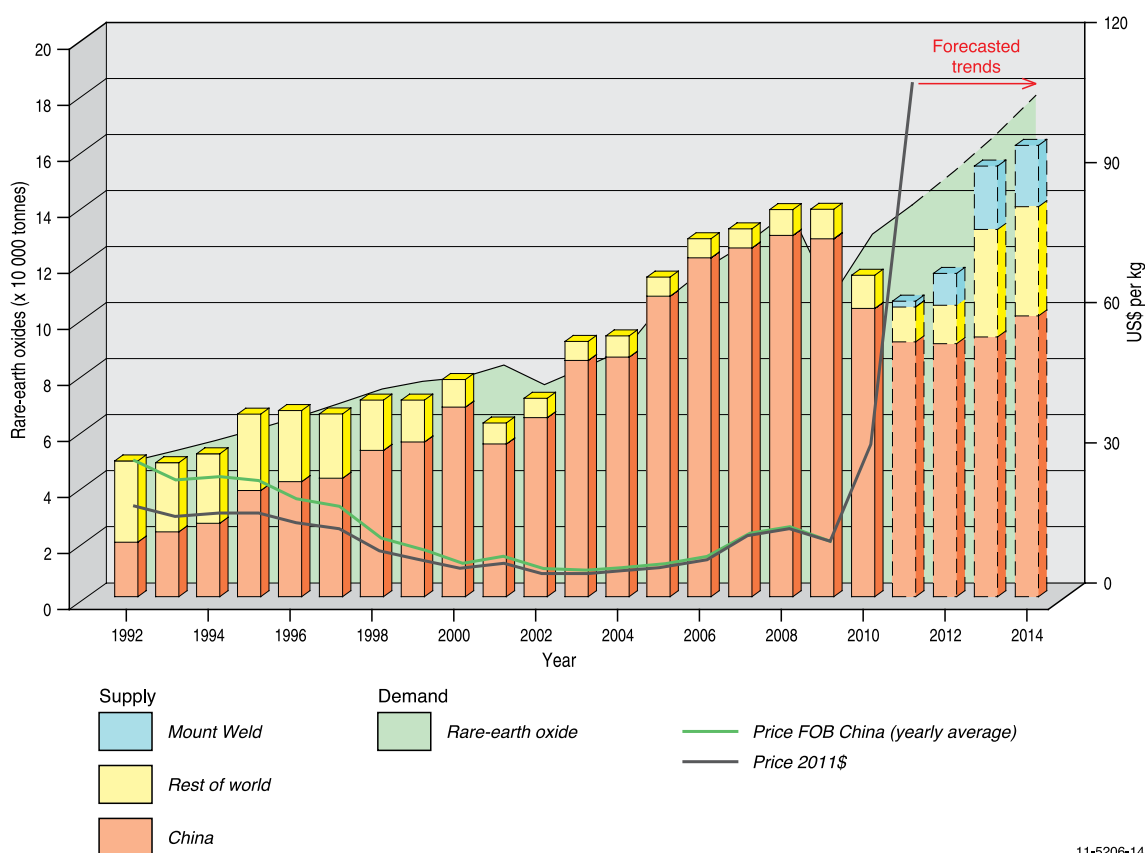


Figure 1.10. Historical and forecasted global supply, demand, and pricing trends of rare-earth oxides, 1992 to 2014. Modified from Lynas Corporation Limited (2011).

1.5. AUSTRALIA'S RESOURCES

Geoscience Australia estimated in 2010 that Australia's REO resources amounted to 1.65 million tonnes of Economic Demonstrated Resources (EDR: [Appendix 5](#)), 0.37 million tonnes Paramarginal Resources, and 34.48 million tonnes in the Submarginal Resources categories (Miezitis, 2010: [Appendix 5](#)). There is a further 24.56 million tonnes in the Inferred Resources category³. About 53 million tonnes of the Submarginal and Inferred Resources are in the Olympic Dam iron oxide-copper-gold deposit in South Australia (predominantly 0.2% La and 0.3% Ce) and are not currently economic. Small quantities of scandium (4620 t Subeconomic and 1690 t Inferred Sc) were also reported in 2010. In addition, about 4160 tonnes of Paramarginal Resources and 51 980 tonnes of Inferred Resources of scandium were reported as REE.

Very significant resources of REE are contained in the monazite component of heavy-mineral sand deposits, which are mined for their ilmenite, rutile, leucoxene, and zircon content. Monazite is a REE-thorium-bearing phosphate mineral found within heavy-mineral sand deposits in Australia. Geoscience Australia estimates Australia's monazite resources to be in the order of 6.1 million tonnes (Miezitis, 2010). Assuming the REO content of monazite to be about 60%, the heavy

mineral deposits could hold a REO resource of around 3.65 million tonnes. Currently, extraction of REE from monazite is not viable because of the cost involved with the disposal of thorium (Th) and uranium (U) present in the monazite.

In a global context, Australia is well placed in the near future to have a significant impact on the potential supply of REO. [Figure 1.11](#) shows that the Mount Weld (WA), Nolans Bore (NT), and Dubbo Zirconia (NSW) projects are well advanced with their development phases (at least to basic engineering status), and in the case of Mount Weld, of high *in situ* commodity value, compared to other operations in the USA, Africa, and Canada. In addition, the Dubbo Zirconia project despite its smaller relative production volume and value, contains the highest percentage (~60%) of the more valuable HREO relative to the other projects shown in [Figure 1.12](#). The other eight projects shown in [Figure 1.12](#) have HREO components less than 17%, with Mount Weld and Nolans Bore having HREO components of 3% and 4%, respectively.

[Figures 1.13](#) and [1.14](#) show some of the concentration and kiln components at the Mount Weld operations in Western Australia and Malaysia. This planned engineering infrastructure timeframe for Mount Weld is highlighted in [Figure 1.11](#).

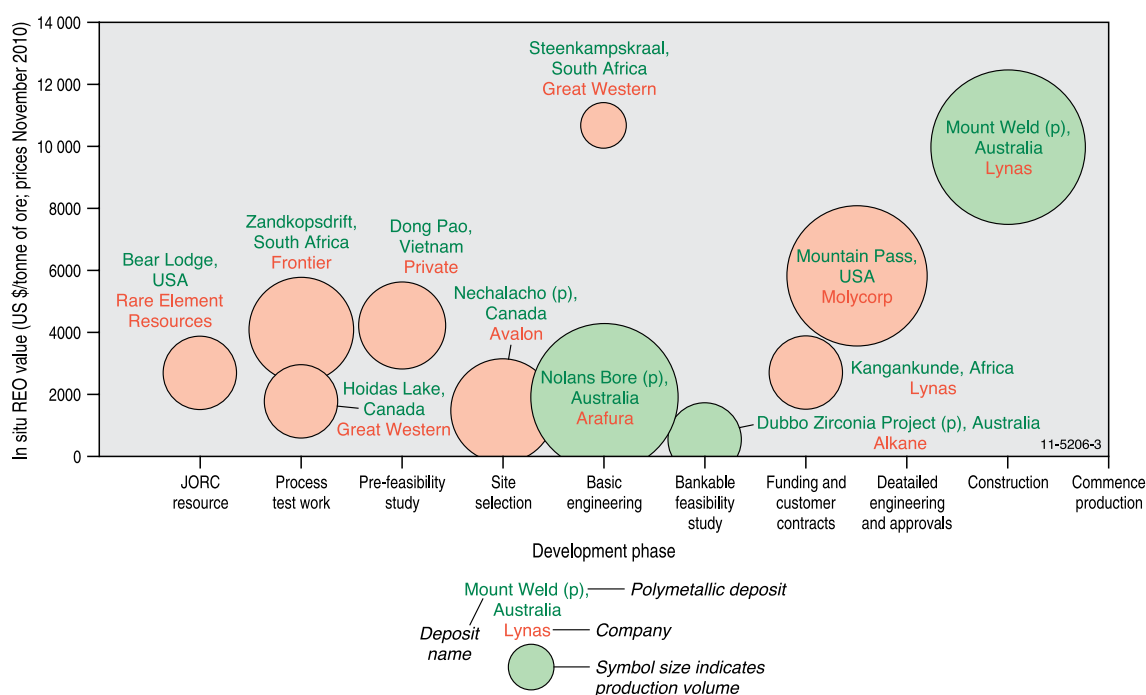


Figure 1.11. Relative value and development phase of major rare-earth-element projects. Australian projects are indicated by green spheres, and other projects by orange spheres. Modified from Lynas Corporation Limited (2011).

³ Definitions of these resource terms are explained in [Appendix 5](#)

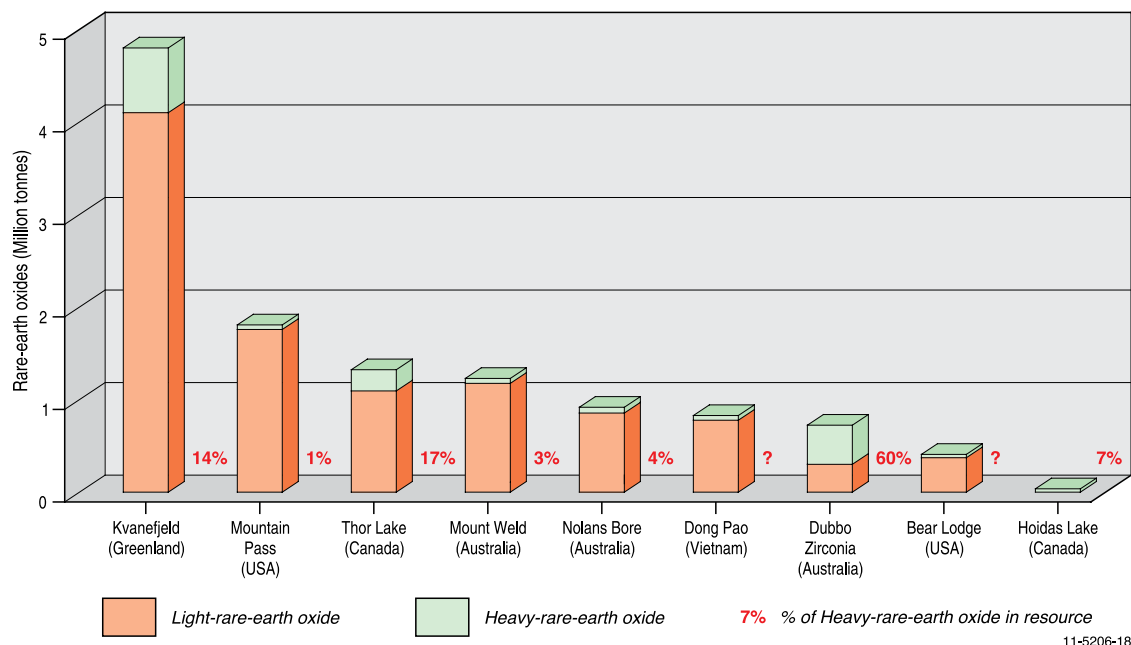


Figure 1.12. Relative percentage (shown in red numbers) of the heavy-rare-earth oxide component in deposits from Australia and elsewhere. Data from the Industrial Minerals Company of Australia Proprietary Limited (IMCOA).

1.6. EXPLORATION HISTORY OF RARE-EARTH ELEMENTS IN AUSTRALIA

Small-scale production of REE has taken place in Australia although information records on this activity are incomplete. REE-bearing minerals (monazite and xenotime) were produced as heavy mineral by-products from beach sand mining and as a very minor contribution from tin mining mainly in Tasmania. Australia was formerly the world's largest producer of monazite, almost entirely from beach sand deposits in Western Australia, New South Wales, and Queensland (Harben and Kužvart, 1996). During the 1970s and 1980s, Australia produced about 12 000 tonnes of

monazite annually and, intermittently, about 50 tonnes per year of xenotime, largely from Western Australia as a by-product of beach sand mining (Cassidy et al., 1997). Production peaked in 1985, with 18 735 tonnes of monazite being mined. Australia's production of monazite (265 000 tonnes from 1952 to 1995) accounted for more than 50% of the world's total production (Towner et al., 1987).

Up to the mid-1990s, Australia was producing and exporting significant quantities of monazite, principally to Europe (Appendix 6). For example, in 1987, Australia supplied about 70% of the concentrates processed by western world producers. Some 98% of all monazite sold from Australia was exported to France. Cassidy et al. (1997) note that environmental issues



Figure 1.13. Filer press and thickener area at concentration plant, Mount Weld Project, Western Australia. Photographs provided by Georgia Bunn (Lynas Corporation Limited: <http://www.lynascorp.com/>)



Figure 1.14. Installation of rotary kilns, Mount Weld Project, Malaysia. Photographs provided by Georgia Bunn (Lynas Corporation Limited: <http://www.lynascorp.com/>)

in Europe were going to have an abrupt impact on the Australian REE industry. In March 1994, because of the increased sensitivity in France to toxic and radioactive waste disposal, a major French chemical and pharmaceutical company (Rhône-Poulenc) closed its monazite processing plant since it was unable to obtain a permit for a disposal site. In addition, the high disposal cost of thorium was considered prohibitive for the extraction of REE from the monazite. Consequently, imports of monazite were stopped, which in turn terminated Australian monazite mining activities in 1995. Monazite fractions from beach sand mining were subsequently returned to the mine site.

Appendix 6 provides annual statistics for the production of monazite in Australia for the period 1980 to 1995. Further historical production statistics can be found in Barrie (1965), Cassidy et al. (1997), and Towner et al. (1996).

During the latter half of the last century, a number of minor occurrences of REE were found in a variety of hard-rock environments throughout Australia. Such occurrences include the uranium deposits of Mary Kathleen in Queensland and Radium Hill in South Australia, and scandium was reported in some Australian tin (cassiterite) and tungsten (wolframite) deposits (Barrie, 1965). One of the earliest documented examples of hard-rock mining of REE in Australia is from a pegmatite in the Coongong region near

Marble Bar, Western Australia. Minor amounts of yttrium-bearing ores were obtained from the pegmatite in 1913, but as typical of these small vein- and dyke-like deposits, production was restricted to only a few years due to low grades and/or tonnage. Barrie (1965) reports that ~1 ton of gadolinite was produced in 1913, and another similar amount of the same mineral is said to have been produced in 1920. With the exception of the beach sand mining described above, and the minor REE contributions from Coongong and monazite concentrates from Tasmania, there has been no historical commercial production of REE in Australia. However, in recent years, considerable exploration interest has been generated by much larger deposits associated with carbonatite (Mount Weld, WA) and trachyte (Toongi, NSW) intrusions, and apatite-bearing veins (Nolans Bore, NT). For example, the Mount Weld deposit has exceptionally high grades up to 13.8% REE and is the world's richest lanthanide deposit. Australia's impact on the global scene of REE from hard-rock sources has historically been insignificant, however, this will change when new deposits, such as Mount Weld and Nolans Bore, commence production.

Appendix 7 summarises the exploration activities and major events, both historical and current, for the REE industry in Australia.

How much are rare-earth elements worth?

The prices of REO prices show significant variance in the relative market value for selected elements. There have been dramatic increases in metal prices for the REO, with cerium oxide (4340%), lanthanum oxide (3940%), and samarium oxide (3235%) recording some of the largest increases since 2007. The prices are dependent on the purity level, which is largely set by the specifications for each application. The table below shows the average annual price for a 'standard' 99% purity of individual elements. Prices are quoted in US\$/kg.

Prices US\$/kg					
Rare-earth oxide	2007	2008	2009	2010	02/05/2011
Lanthanum oxide	3.44	8.71	4.88	52.49	139.00
Cerium oxide	3.04	4.56	3.88	52.62	135.00
Neodymium oxide	30.24	31.90	19.12	81.38	225.00
Praseodymium oxide	29.05	29.48	18.03	78.62	208.00
Samarium oxide	3.60	5.20	3.40	36.58	120.00
Dysprosium oxide	89.10	118.49	115.67	287.85	705.00
Europium oxide	323.90	481.92	492.92	611.54	1200.00
Terbium oxide	590.40	720.77	361.67	620.38	1200.00

Metal prices from Lynas Corporation Limited at: http://www.lynascorp.com/page.asp?category_id=1&page_id=25