Mineral Commodity Report 17 - Rare Earths and Related Elements

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Definition

The rare-earth elements (REE) are the 15 lanthanide elements with atomic numbers 57 through 71 that are in Group IIIA of the Periodic Table: lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The REE are represented by the single square of lanthanum in the main part of the Periodic Table and listed in a separate sub-table below the main groupings (Fig. 1). Yttrium (atomic number 39), a Group IIIA transition metal, although not a lanthanide is generally included with the REE as it occurs with them in natural minerals and has similar chemical properties. Commonly included with the REE because of their similar properties, are scandium (atomic number 21), also a Group IIIA transition metal, and thorium (atomic number 90), an element in the actinide series of the Periodic Table.

Figure 1: Periodic table with the REE (light shading) and scandium, yttrium and thorium highlighted.

REE are classified into two groups: the light or cerium subgroup, comprising the first seven elements (atomic numbers 57-63) and thorium; and the heavy or yttrium subgroup, comprising the elements with atomic numbers 64-71 as well as yttrium and scandium. Despite its low atomic weight, yttrium is categorised with the heavy REE

	Symbol	Atomic no.	Atomic wt.	Density	Valence	Melting point (ºC)	Boiling point (ºC)	Crustal abundance (ppm)	Crustal abundance order	Preferred analysis method	Routine detection limit (ppm)
Lanthium	La	57	138.9	6.15	3	918	3464	30	28th	MS	0.1
Cerium	Ce	58	140.12	6.77	3, 4	798	3443	60	26th	MS	0.1
Praseodmium	Pr	59	140.98	6.64	3	931	3520	7	37th	MS	0.05
Neodymium	Nd	60	144.24	7.01	3	1021	3074	25	27th	MS	0.1
Promethium	Pm	61	145	7.26	3	1042	3000	4.5×10^{-20}			
Samarium	Sm	62	150.4	7.52	3	1074	1794	5	40th	MS	0.1
Europium	Eu	63	151.96	5.2	2, 3	822	1527	1	50th	MS	0.05
Gadolinium	Gd	64	157.25	7.9	3	1313	3273	4	41st	MS	0.1
Terbium	Tb	65	158.93	8.23	3	1356	3230	0.7	58th	MS	0.05
Dysprosium	Dy	66	162.5	8.55	3	1412	2567	3.5	42nd	MS	0.1
Holmium	Ho	67	194.93	8.8	3	1474	2700	0.8	55th	MS	0.05
Erbium	Er	68	167.26	9.1	3	1529	2868	2.3	43rd	MS	0.1
Thulium	Tm	69	168.93	9.34	3	1545	1950	0.32	61st	MS	0.05
Ytterbium	Yb	70	173.04	7	3	819	1196	2.2	44th	MS	0.1
Lutetium	Lu	71	174.97	9.84	3	1663	3402	0.4	59th	MS	0.05
Scandium	Sc	21	44.96	3	3	1541	2836	8	36th	NAA	0.5
Yttrium	Y	39	88.91	4.47	3	1522	3338	30	29th	MS	1
Thorium	Th	90	232.04	11.8	4	1750	4850	6	39th	NAA	1

MA= mass spectroscopy
NAA = neuron activation

because its properties are closer to those of the heavier REE than to the lighter group.

The geochemical behaviour of the REE during specific geological processes, for example their partitioning in igneous systems and their relative immobility during hydrothermal alteration, has made them particularly suitable for determining the origin of igneous rocks. Specific REE isotopes are also used in geochronology. These applications have led to a wealth of literature on REE, and recent reviews by Lipin and McKay (1989) and Jones *et al.* (1996) are excellent initial references for information on the mineralogy, geochemistry and occurrence of REE.

Discovery and origin of names

The history of the discovery and naming of the REE was reviewed by Habashi (1994a, 1994b) and is summarised in Table 1. The term rare earths was suggested by Johann Gadolin in 1794: "rare" because when the first of the REE were discovered they were thought to be present in the earth's crust only in small amounts, and "earths" because as oxides they have an earthy appearance. The numerous chemical similarities between the REE meant that it took more than a century from the first discovery to complete isolation and classification. Significant production of REE began in the 1880s, with mining of the mineral monazite in Brazil.

Major ores and minerals

Despite their name, the REE are in fact not especially rare. Each is more common in the earth's crust than silver, gold or platinum, while cerium, yttrium, neodymium and lanthanum are more common than lead. The light REE (La through Eu) are more abundant than the heavy REE (Gd through Lu), and furthermore, the elements of even atomic number are more abundant than their neighbours of odd atomic number, because of the greater relative stability of nuclei with even atomic number compared to those with odd atomic number.

REE are never found as free metals in the earth's crust and all their naturally occurring minerals consist of mixtures of various REE and nonmetals. Bastnaesite, monazite and xenotime are the three most economically significant minerals of the more than 200 minerals known to contain essential or significant REE (Tables 2 and 3; see Appendix A of Jones *et al.*, 1996 for an extensive list of minerals and their formulae). Bastnaesite and monazite are sources of the light REE and account for about 95% of the REE currently utilised. Monazite is also the principal ore of thorium, containing up to 30% Th, which together with smaller (up to ~1%) quantities of U imparts radioactive properties to the monazite. Xenotime and minerals such as allanite are a source of the heavy REE and yttrium.

Bastnaesite occurs predominantly in calc-silicate rich rocks related to alkaline intrusive igneous complexes, and to a lesser extent, in quartz veins, epithermal fluorite-bearing veins and breccia fillings (Gieré, 1996). Monazite and xenotime occur as accessory minerals in low-Ca granitoid rocks and pegmatites. Following weathering of these rock types, monazite and xenotime are concentrated in heavy mineral placer deposits because of their resistance to chemical attack and high specific gravity. Xenotime is commonly associated with zircon, being isostructural and often found enclosing zircon.

Other commercial sources of REE are apatite (Commonwealth of Independent States), REE-bearing clays ("Longnan 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 allanite (containing Ce and Y), zircon (Th, Y and Ce), euxenite and loparite. The main commercial source of scandium is as a by-product from the processing of uranium and tungsten.

Properties

The REE are metals, with high lustre and electrical conductivity. In colour, they are typically silver, silvery-white or grey. Chemically, REE are strong reducing agents and their compounds are generally ionic. Most of the REE are trivalent, with europium also having a valence of +2 and cerium also a valence of +4. Europium, followed by

Year	Element	Origin of name	Discovery	Nationality	
1794	Yttrium	Ytterby mine, Sweden	Gadolin	Finn	
1803	Cerium	After the asteroid Ceres (which in turn named after a Greek deity)	Baron Jons Jakob Berzelius and Willaim Hisinger	Swedish	Also discovered independently in same year by Martin Heinrich Klaproth (German). The pure element was not isolated until 1875.
1828	Thorium	After Thor, the Scandinavian god of war	Baron Jons Jakob Berzelius	Swedish	
1839	Lanthanum	From Greek lathano = to lie hidden (because it lay concealed in the earth)	Carl Gustav Mosander	Swedish	
1843	Erbium	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish	

continued

Year	Element	Origin of name	Discovery	Nationality	
1878	Terbium	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish	
1878	Ytterbium	Derived from Ytterby mine, Sweden	Jean Charles de Marignac	French	In 1907 and 1908, Georges Urbain (French) and Carl Auer von Welsbach (Austrian) independently separated Marignac's ytterbium into two elements, which are now called ytterbium and lutetium
1879	Samarium	After the mineral samarskite, in turn after the minerals discoverer, a Russian mining official V.E. Samarsky	Paul E. Lecoq de Boisbaudran	Swedish	
1879	Scandium	After Scandinavia	Lars Fredrik Nilson	Swedish	
1879	Holmium	After the Latin for Stockholm, Holmia	Per Teodor Cleve	Swedish	Discovered independently by Jacques Louis Soret and Marc Delafontaine (Swiss)
1879	Thulium	From the Latin Thule, an ancient name for Scandinavian	Per Teodor Cleve	Swedish	
1880	Gadolinium	In honour of Johan Gadolin, a Finnish chemist	Jean de Marignac	Swiss of French origin	Paul E. Lecoq de Boisbaudran independently isolated the element from Mosander's "yttria" in 1886
1885	Praseodymium	From Greek prasios = green, in reference to the colour of the salts, and didymos = twin, because the earth didymia was separated into two salts; Pr and Nd	Carl Auer von Welsbach	Austrian	
1885	Neodymium	From Greek neo = new and didymos = twin, because the earth didymia was separated into two salts; Pr and Nd	Baron Carl Auer von Welsbach	Austrian	Not isolated in relatively pure form until 1925
1886	Dysprosium	From Greek dys = bad and prositos = approachable, dys-prositos means hard to get because of the difficulty involved in its detection and isolation	Paul E. Lecoq de Boisbaudran	French	
1896	Europium	After Europe	Eugene Demarcay	French	
1907	Lutetium	After Lutetia, Latin name for the place where Paris was founded	Independently by Georges Urbain and Carl Auer von Welsbach	French and Austrian	
1945	Promethium	After Prometheus, in Greek mythology, who brought fire to mankind in reference to harnessing of the energy of the nuclear fisson and warning against its dangers	Charles DuBois Coryell, Lawrence E. Glendenin and Jacob A. Marinsky	American	

Table 1: Discovery and origins of names of the REE (modified after Table 1 of Habashi, 1994a).

Name, formula Colour	Hardness	Density	Lustre	Crystal form	Transparency	Discoverer	Year	Location
Allanite (epidote group) $CaCe(Fe^{2+}Al_2)(SiO_4)_3(OH)$ or $CaY(Fe^{2+}Al_2)(SiO_4)_3(OH)$ black to dark brown	5-6	3-4	resinous or pitchy submetallic	monoclinic	translucent to opaque	T. Allan Thomson	1808 1810	East Greenland
Apatite $(Ca,Na,Ce,Th)_5(P,Si,S,Bi)_3O_{12}(F,OH,Cl,O)$ green or brown, less commonly violet, blue, yellow or colourless	5	3.15-3.20	subresinous-vitreous	hexagonal	transparent to opaque			
Bastnaesite $(Ce,La)(CO_3)F$ yellow to reddish brown	4-4.5	4.9-5.2	vitreous to greasy	hexagonal	transparent to translucent	W. Hisinger	1838	Bastnas mine, Sweden
Brannerite $(U,Th,Ca,Y)(Ti,Fe)_2O_6$ black	4.5-5.5	4.5-5.4	vitreous	monoclinic	translucent to opaque	Hess and Wells	1920	Kelly Gulch, Idaho
Cerite $Ce_9(Ca)Fe^{3+},Mg)(SiO_4)_6[SiO_3(OH)](OH)_3$ brown, or cherry red to grey	5.5	4.8	resinous	tetragonal or orthorhombic		Contedt, Bergman; named by Berzelius	1751	Bastnas mine, Sweden
Euxenite $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ brownish black	5.5-6.5	5-5.9	submetallic, or less commonly vitreous or resinous	orthorhombic	opaque	B.M. Keilhan	1840	Jolster, Norway
Fergusonite $(Y,Ce,U,Th,Ca)(Nb,Ta,Ti)O_4$ brownish black	5.5-6.5	5.4 (4.2-7.5)	vitreous, submetallic	tetragonal	opaque	Giesecke	1806	Kikertaursuk, Greenland
Florencite $REEAl_3(PO4)_2(OH)_6$ colourless to pale yellow	5-6	3.5		trigonal	translucent to transparent			Minas Geraes, Brazil
Gadolinite $Be_2FeY_2Si_2O_{10}$ black, greenish black or brown	6.5-7	4.0-4.5	vitreous to greasy	monoclinic	translucent to transparent	Arrhenium; named by Klaproth	1788	Ytterby mine, Sweden
Huttonite $ThSiO_4$ colourless to very pale cream				monoclinic	translucent to transparent	A. Pabst & C.O. Hutton	1951	Westland, New Zealand
Loparite (Niobium perovskite) $(Ca,Ce,N)_2(Nb,Ti)_2O_6$ brown to black	5.5	4.77	adamantine, metallic adamantine, metallic or dull	orthorhombic	transparent to opaque	I. Kusnezov	1925	Kola peninsula, Russia
Monazite $(Ce,La,Nd,Th)PO_4$ $(REE)PO_4$ yellowish to brown	5-5.5	4.6-5.4	resinous to waxy	monoclinic	transparent to translucent	Levy; named by A. Breithaupt	1823	Miask, Ural
Thorite $ThSiO_4$ black, brown, some orange-yellow	4.5-5	4.5-6.7	vitreous, resinous to greasy	tetragonal	translucent to opaque	J.J. Berzelius	1829	near Brevik, Norway
Uranthorite $(U,Th)SiO_4$ dirty brown to olive-yellow	4-5	6.7	vitreous to resinous	tetragonal	translucent to opaque	P. Collier	1880	Champlain iron region, New York State
Xenotime YPO_4 yellow-brown	4-5	4.4-5.1	vitreous to resinous	tetragonal	translucent to opaque	J.J. Berzelius	1824	Ytterby mine, Sweden
Zircon $ZrSiO_4$ colourless, grey, reddish brown, greenish or yellow	7.5	4.6-4.7	vitreous to adamantine	tetragonal	transparent to opaque	known in antiquity, but first named as zircon by Werner	1783	Ceylon

Table 2: Properties of some REE minerals and history of their discovery (partly after Table 5 of Habashi, 1994a).

cerium, are the most reactive elements of the REE. REE tend to tarnish rapidly in air, forming rare earth oxides (REO). At elevated temperatures many ignite and burn vigorously, e.g. europium ignites in air at about 150 to 180ºC. Most REE compounds are strongly paramagnetic, and holmium is one of the most paramagnetic substances known. Many REE compounds, particularly those of europium, praseodymium and neodymium, strongly fluoresce under ultraviolet light. Promethium and thorium are radioactive.

Mischmetal, an alloy composed of iron and REE, is pyrophoric and when scratched it gives off sparks capable of igniting flammable gases, a property utilised in its application as flints in cigarette lighters, miners' safety lamps, and automatic gas-lighting devices.

Formation

REE are found mainly in primary deposits associated with igneous intrusions and associated veins, dikes and pegmatites, and secondary deposits of beach, dune, and alluvial placers. Residual deposits are also known and may be economically important in the future.

Carbonatite associated deposits

Carbonatites, igneous rocks comprising more than 50% modal carbonate, characteristically contain higher levels of REE (e.g. 0.37%, 0.42% and 1% for calcio-, magnesio-, and ferrocarbonatites respectively) than almost all other rock types, and they are the world's main source of REE. The REE-bearing carbonatites are typically the last magmatic stage in alkaline-carbonatite complexes (e.g. syenites, nepheline syenites and nephelinites). The REE

carbonatite deposits are subdivided into magmatic and metasomatic types (Richardson and Birkett, 1996a). Magmatic deposits are formed through processes associated with primary magmatic crystallisation. REE are generally concentrated during fractional crystallisation into the last in a series of carbonatite differentiates, typically ferro-carbonatites (iron-rich dolomite or ankerite carbonatites). Magmatic carbonatite deposits generally occur in small (3-4 km diameter) plug-like bodies in composite plutons with coeval mafic and ultramafic rocks. Mineralisation is commonly related to magmatic layering and flow structures within the host rocks. The deposits are commonly groups of lenses or irregular shoots that, in plan, have crescent-shaped or annular forms. In section, these deposits generally have steep dips, parallel to the walls of the intrusive complex.

Metasomatic deposits (Richardson and Birkett, 1996a; Birkett and Sinclair, 1998) form by the reaction of fluids released during crystallisation with pre-existing carbonatite or country rocks producing hydrothermal alteration and/or skarn minerals. The hydrothermal alteration is characterised by alkali metasomatism or fenitization where pre-existing minerals are replaced by alkai feldspar, and sodic pyroxene and amphibole minerals. Metasomatic deposits typically have the form of: 1) dikes and dilatant veins of ankerite or dolomite, with or without calcite; 2) thin hydrothermal veins; 3) stockworks; and 4) replacement bodies rich in calcite and dolomite or ankerite. Concentrations of REE in these rocks are about 1-3 wt% and require further concentration by low temperature hydrothermal alteration and/or weathering to form an economic deposit.

Element	Bastnaesite (Mountain Pass)	Monazite (Capel, WA)	Xenotime (Lahat, Perak)	Longnan clay (Xunwu, Jiangxi Province)	Loparite (Russia)
Lanthanum	33.20	23.89	1.24	43.37	25
Cerium	49.10	46.02	3.13	2.38	53
Praseodymium	4.34	5.04	0.49	9.02	6
Neodymium	12.00	17.38	1.59	31.65	14
Samarium	0.79	2.53	1.14	3.90	0.9
Europium	0.12	0.05	0.01	0.50	0.08
Gadolinium	0.17	1.49	3.47	3.00	0.56
Terbium	0.02	0.04	0.91	trace	0.37
Dysprosium	0.03	0.69	8,32	trace	0.12
Holmium	0.01	0.05	1.98	trace	0.08
Erbium	0.00	0.21	6.43	trace	0.016
Thulium	0.00	0.02	1.12	trace	0.003
Ytterbium	0.00	0.12	6.77	0.26	0.008
Lutetium	0.00	0.04	0.99	0.10	0.002
Yttrium	0.09	2.41	61.00	8.00	0.008
Total	99.86	99.98	98.59	102.18	100.147

Table 3: Individual REE content of some commercial REE minerals expressed as a percentage of total REE content (modified after Table 147 of Harben and Kuzvart, 1996).

The most abundant minerals in carbonatite deposits are the three fluorocarbonate minerals bastnaesite, parisite and synchysite; the hydrated carbonate, anacylite; and the phosphate monazite. Heavy REE minerals are rare.

Major sources are the Mountain Pass deposit in southern California and Bayan Obo in Inner Mongolia, People's Republic of China. Mountain Pass has consistently been the world's leading producer of light REE concentrates over the past few decades. Discovered in 1949, this deposit contains some 36 Mt at 7.67% rare earth oxides (REO). The main orebody in the Sulphide Queen Mine is a tabular-shaped carbonatite up to 200 m wide and 730 m long and consists of 40-75% calcite, 15-50% barite, and 5-15% bastnaesite/parisite. Bayan Obo was discovered in 1927 and explored on a large scale from the 1950s. It is the world's largest known REE deposit with 48 Mt at an average grade of 6% REO in stockwork and carbonate replacement bodies of magnetite-hematite ore (Drew *et al.*, 1990). The mined product is split into two fractions, one for the iron smelter and the other, containing both bastnaesite and a thorium-deficient monazite, for processing to a 60% REO concentrate. Other carbonatites rich in REE are known at the Mineral Hill District, Idaho-Montana, in the USA; Oka, Quebec, Canada (23.8 Mt at 0.2-0.5% REO); Araxa and Tapira, Minas Gerais, Brazil; Tomtor, in northern Siberia; the Fen District, Norway; Koronge, Burundi; and Kangankunde Hill, Malawi.

Peralkaline rock associated deposits

Peralkaline igneous rocks are characterised by a molar excess of alkali elements ($Na_2O + K_2O$) over aluminium (Al_2O_3), resulting in the occurrence of alkali amphibole and pyroxene minerals. Magmatic and metasomatic REE mineralisations are generally associated with small satellite phases of peralkaline batholiths (Richardson and Birkett, 1996b; Birkett and Sinclair, 1998). In the magmatic deposits, the principal REE-bearing minerals crystallised with their host igneous rocks and are typically found disseminated throughout specific igneous units. Hydrothermal alteration associated with the deposits is generally late deuteric and local in nature, and characteristically there are no extensive zones of hydrothermal alteration surrounding the deposits.

Metasomatic deposits occur in or near peralkaline igneous rocks, and are superimposed on pre-existing rocks. The deposits are related to the cooling and fluid release of intrusions; hydrothermal alteration may be extensive.

Magmatic deposits assume the form of the host intrusive body, whereas metasomatic deposits range in form from veins and stockworks to irregular replacement zones in which minerals are typically fine grained and widely disseminated. Subvolcanic analogues of the intrusive deposits are pegmatite-aplite dikes and veins vented from the roof zones of nearby peralkaline intrusive bodies.

Examples include the Khibini and Lovozero complexes in the Kola Peninsula of Russia; Brockman deposit, Western Australia; Pajarito Mt, New Mexico; Thor Lake, Northwest Territories, Canada (the Lake Zone has 64 Mt at 1.99% REO); Strange Lake/Lac Brisson, Labrador-Quebec, Canada (open pit mineable reserve of 52 Mt with 0.54% REE, 0.31% Y_2O_3); and Oslo region, Norway.

Olympic Dam hematitic granite breccia type deposits

REE mineralisation is a component of Proterozoic iron oxide (Cu-U-Au-REE) deposits such as Olympic Dam (e.g. Hitzman *et al.*, 1992; Oreskes and Hitzman, 1993). The mineralisation is hosted in hematitic granitic breccias of late Precambrian age that were formed by a variety of hydrothermal, magmatic, sedimentary and tectonic processes in a continental rift setting. At Olympic Dam a very large orebody of disseminated chalcopyrite-bornite-chalcocite is accompanied by gold, uranium, silver, rare earths, barium and fluorine minerals. The deposit averages 1.6% Cu, 0.05% U, 3.5 g/t Ag, 0.6 g/t Au and 35% Fe, and contains notable amounts of REE, in particular 0.2% La and 0.3% Ce.

Skarn deposits

Skarn deposits are epigenetic, metasomatic deposits which form in carbonate-rich rocks within the contact aureoles of intrusions (Birkett and Sinclair, 1998). In addition to skarn deposits associated with carbonatites mentioned above, 200,000 t of REO (dominantly light REE) were produced from the Mary Kathleen U-REE-Th skarn in Australia, now mined out. The deposit formerly held 9.5 Mt of ore at an average grade of 0.13% U_3O_8. The skarn occurs in garnet-bearing calc-silicate rocks adjacent to an alkali-granite intrusion. The main ore mineral is uraninite, and REE are hosted in uraninite, apatite and allanite.

Placer deposits

Resistant REE minerals of high specific gravity, particularly monazite and xenotime, are found concentrated in placer deposits that are exploited mainly for their titanium and zirconium values. As a result, the production level of monazite and xenotime is dependent on other markets. The main producers are beach sand deposits of Western Australia (Eneabba, Yoganup and Capel), India (Alwaye, Kerala State) and Sri Lanka which are mined mainly for ilmenite and rutile (e.g. see Mineral commodity report 16 - titanium; Christie and Brathwaite, 1998). Monazite and xenotime have also been produced as byproducts of placer tin mining in Thailand, Malaysia and Indonesia.

Residual deposits

Laterites
REE laterite deposits are formed by intense subtropical weathering of REE-rich alkaline complexes. They consist predominantly of mineral assemblages of goethite, hematite, Al-hydroxides, kaolinite minerals and quartz, and typically contain 10-25 wt% REO, but up to 42 wt% REO have been reported from laterites on the Mt Weld alkaline carbonatite complex in Western Australia. REE in laterites are predominantly bound in residual magmatic apatite, pyrochlore and monazite, or in secondary phosphate minerals of the crandallite group, secondary apatite and monazite, plumbogummite, rhabdophane and/or iron hydroxides. Examples include Araxa and Catalao in Brazil; Mt Weld in Australia; Mabounie in Gabon; and Lueshe in Zaire.

Other residual deposits
REE-bearing clay, termed Longnan, ionic or ion-adsorption type ore, is mined in Jiangxi Province, Southeast China. The ore has formed from the weathering of granite and

typically grades about 1% REO. It is characterised by a very low cerium content (0.3-1.7% in grade A, and 3-5.5% in grade B) and a REO content which is rich in samarium, europium, and terbium, or in yttrium (Harben and Kuzvart, 1996).

Residual deposits are associated with carbonatites in Mombassa, Kenya, and in Minas Gerais, Brazil. Apatite is found in phosphate rock, as in the Phosphoria Formation of the western USA and in the Florida phosphate districts.

Uses

Because of their similarity, REE are difficult to separate and initial applications were based on "group" properties of a mixture of several of the elements. Thorium, along with associated REE, was first used in the 1800s in the manufacture of incandescent gas mantles. Other early uses of REE were in lighter flints, arc carbons, polishing compounds, and glass and ceramic additives. Mischmetal alloy, composed of 51-53% Ce, 22-25% La, 15-17% Nd, 3-4% Pr, 2-3% Sm, 3% Tb, 3% Y, and 5% Fe, is mainly used in the production of lighter flints and high-strength low-alloy steel.

Current uses of REE, summarised in Table 4, are about 95% in the mixed form, on a volume basis, with the individual elements accounting for the remaining 5% (Gschneidner, 1989).

Worldwide, about 35% of REE are used as catalysts, mainly in the refining of crude oil. For example, addition of 1 to 5% REE chloride to a zeolite catalyst increases the catalysts cracking efficiency. REE are also included in catalytic converters in automobiles, where REE stabilise the gamma-alumina support and enhance the oxidation of pollutants.

Approximately 30% of the REE are used in the glass/ceramics industry as glass-polishing compounds, decolourising agents, UV absorbers and antibrowning agents, glass and ceramic colouring agents, additives to structural ceramics such as stabilised zirconia and silicon nitride Si_3N_4, and in optical lenses and glasses.

About 30% are used in metallurgy as an alloying agent to desulphurise steels, as a nodularising agent in ductile iron, as lighter flints and as alloying agents to improve the properties of superalloys and magnesium, aluminium and titanium alloys. A rapidly expanding application is in batteries. Mischmetal is a component of nickel metal hydride batteries that are replacing nickel cadmium batteries in powering portable electronic equipment such as lap top computers and mobile phones.

The individual elements account for the remaining 5% of volume but over 50% of the monetary value. A currently expanding application for REE is in the production of permanent magnets. Samarium-cobalt ($SmCo_5$-Sm_2Co_{17}) permanent magnets are used in industrial, military and aerospace applications, whereas less costly neodymium-iron-boron ($Nd_2Fe_{14}B$) magnets are used in automobile starting motors, windscreen wiper motors and other mechanisms, medical magnetic imaging and industrial motors, compact disc players, computer disk drives, personal stereos, and camera motors. Other industrial uses include: phosphors in colour TV and fluorescent lighting,

garnet bubble storage devices, oxygen sensors, microwave ferrites and garnets, fibre optics, synthetic crystals used in lasers (especially Nd), lanthanum-nickel alloy for hydrogen storage, and gallium-gadolinium-garnet (GGG) as a memory film in computers. REE are used in the nuclear industry in control rods, as dilutants, and in shielding, detectors and counters. Thorium is a potential atomic fuel source.

Price

Prices for REOs have generally fallen since 1995 because of the rapid expansion of Chinese production, however, because of increasing demand for REOs, prices are expected to increase. In mid 1998, bastnaesite concentrate (70% leached) was US$1.40 per lb of REO and yttria (99.99% Y_2O_3) was US$25-28 per kg (Industrial Minerals, August 1998 issue). Table 5 lists some prices for individual REE and products.

World production and consumption

World mine production of REE is dominated by China and the USA, and totalled an estimated 79,500 t REO content in 1997, consisting of 70,000 t REO in bastnaesite production (China 50,000 t REO including ion adsorption ores, xenotime and monazite, and USA 20,000 t REO), 6,000 t in loparite production (Commonwealth of Independent States), 3,220 t REO in monazite production (India 2700 t REO, Brazil 400 t REO and Sri Lanka 120 t REO), and 300 t REO in xenotime production (Malaysia) (Satterthwaite, 1998).

During the 1990s, an increasing awareness and enforcement of environmental safety standards has led to a decline in the supply of monazite-derived products, as the present forms of monazite that are mined and processed have a relatively high level of radioactivity. This has led to an increasing proportion of REE products derived from bastnaesite ores or ion adsorption ores.

Apart from in the USA, much of the rare earth material produced is not processed in the country of origin. In fact, in addition to USA, world production of processed REE is dominated by France and Japan, although China is becoming increasingly important. Before 1990, less than 10% of China's total REE production was in the form of separated REE, but by 1997 this had increased to almost 50%. Japan is currently the worlds largest consumer of REE. Total world consumption of REO in 1997 is estimated at 68,500 t, 11,000 t less than 1997 mine production (Satterthwaite, 1998).

Ore processing, smelting and refining

REO is concentrated from bastnaesite ores at Mountain Pass by a hot froth flotation. This produces a 60% REO concentrate that may be upgraded to a 70% concentrate by leaching or to a 90% concentrate by calcining (Harben and Kuzvart, 1996). The cerium-rich concentrate yields cerium oxides and salts, and a cerium-poor lanthanide-rich concentrate used as a feedstock for further processing, either at the mine or in specialised plants around the world.

Monazite is separated from other heavy minerals, usually by wet gravity concentration and then electrostatic and magnetic separation to produce a concentrate with 55-66%

Element	Comment	Applications
Lanthanum	Component of mischmetal.	Ceramic glazes, high quality optical glass, camera lenses, microwave crystals, ceramic capacitors, glass polishing, petroleum cracking.
Cerium	Most abundant REE. Chief component of mischmetal.	Glass polishing, petroleum cracking catalysts, alloys - with iron for sparking flints for lighters, with aluminium, magnesium and steel for improving heat and strength properties, radiation shielding, many others.
Praseodymium		Yellow ceramic pigments, tiles, ceramic capacitors. With neodymium in combination for goggles to shield glass makers against sodium glare, Permanent magnets. Cryogenic refrigerant.
Neodymium	Important in magnetic alloys.	Ceramic capacitors, glazes and coloured glass, lasers, high strength permanent magnets as neodymium-iron-boron alloy, petroleum cracking catalysts.
Promethium	Not found in nature. Radioactive; produced only in nuclear reactors.	Radioactive promethium in batteries to power watches, guided missile instruments, etc, in harsh environments.
Samarium	Important in magnetic alloys.	In highly magnetic alloys for permanent magnet as Samarium-Cobalt alloy; probably will be superseded by neodymium. Glass lasers. Reactor control and neutron shielding.
Europium	One of rarest, and most reactive of rare earths. Absorbs neutrons.	Control rods in nuclear reactors. Coloured lamps, cathode ray tubes. Red phosphor in colour television tubes.
Gadolinium		Solid state lasers, constituent of computer memory chips, high temperature refractories, cryogenic refrigerants.
Terbium	Associated with gadolinium.	Cathode ray tubes, magnets, optical computer memories; future hard disk components; magnetostrictive alloys.
Dysprosium	Absorbs neutrons. Magnetic alloy.	Controls nuclear reactors. Alloyed with neodymium for permanent magnets. Catalysts.
Holmium	Absorbs neutrons.	Controls nuclear reactors; catalysts; refractories.
Erbium	Physical properties almost identical with Holmium and Dysprosium.	In ceramics to produce a pink glaze; infra-red absorbing glasses.
Thulium	Gives x-rays on irradiation in nuclear reactor.	X-ray source in portable X-ray machines.
Ytterbium	Properties very similar to Lutetium - not well known.	Practical values presently unknown. Research.
Lutetium	Chemical and physical properties not well known.	Deoxidiser in stainless steel production, rechargeable batteries, medical uses, red phosphors for colour television, superconductors.
Yttrium	Associated with Holmium, Erbium. Cold or hot forged.	Deoxidiser in stainless steel production, rechargeable batteries, medical uses, red phosphors for colour television, superconductors.
Scandium	Close to Aluminium in chemical and physical properties.	X-ray tubes, catalysts for polymerisation, hardened Ni-Cr superalloys, dental porcelain.
Thorium	Resembles nickel, as soft and as plentiful as lead. Radioactive.	Gas mantles. Can be used as nuclear fuel in place of uranium.

Table 4: Major applications of the REE, yttrium, scandium and thorium (modified after Table 1 of Cooper, 1990).

REO (Harben and Kuzvart, 1996). Both monazite and xenotime are usually cracked by heating the concentrate in an autoclave at 150°C with a 70% NaOH solution (Gschneidner, 1989). After cooling, the addition of H_2O removes the soluble Na_3PO_4, leaving the REE as REO and thorium as $Th(OH)_4$. The REO are dissolved in HCl to form an anhydrous mixed rare-earth chloride, which is reduced electrolytically to make mischmetal or processed further to yield individual REE.

There are a number of methods for extracting and separating the individual REE, including liquid-liquid solvent extraction that is based on differences in affinity of the individual rare earths for a chelating agent in an organic

Product (US$/kg)	Purity (%)	Price range
Cerium carbonate	99	10
Cerium oxide	98-99.99	6-35
Cerium metal	99-99.9	21-35
Dysprosium oxide	99-99.99	50-120
Dysprosium metal	99-99.99	80-185
Erbium oxide	99-99.99	45-230
Europium oxide	99.9-99.999	230-272
Gadolinium oxide	99-99.99	15-40
Lanthanum oxide	99.9-99.999	15-35
Lutetium oxide	99-99.99	2,900-3,900
Mischmetal	>50% Ce	6-8
Neodymium oxide	96-99.99	14-120
Neodymium metal	97-99	23-35
Praeeodymium oxide	96-99.5	7-18
Samarium oxide	96-99.99	13-32
Samarium metal	99-99.9	75-90
Scandium oxide	99-99.999	500-5,750
Terbium oxide	99-99.99	200-415
Terbium metal	99-99.99	500-900
Ytterbium oxide	99.9-99.99	235-265
Ytterbium metal	99-99.9	300-385
Yttrium oxide	99-99.999	15-30
Yttrium metal	99-99.9	80-110

Table 5: End-user prices for REE and speciality metals, July 1998 (supplied by Mineral PriceWatch).

solvent (Harben and Kuzvart, 1996). When the REE in water are mixed with the chelating agent solution, the REE with the highest affinity becomes enriched in the solvent; if repeated sufficiently the concentration builds up to produce a 99.999% pure product. Since this process involves sequential extraction, REE with a specialised market are also produced.

Products for trade include concentrates, individual or mixed compounds, and individual or mixed metal. High purity metals are marketed in the form of sponge, lump, ingot, rod, wire, chips, powder, sheet, foil, plates, sputtering plates, and custom cast and machined shapes. Alloys are available as cast shapes such as balls, donuts, canisters, billets, lumps, and ingots, and are sold in pound to ton lots.

New Zealand occurrence and resources

The occurrence of REE in New Zealand has been reviewed by Officers of the New Zealand Geological Survey (1970; monazite and uranothorite), Williams (1974), and Brathwaite and Pirajno (1993). REE, yttrium, scandium and thorium minerals found in New Zealand include: allanite, cerianite, daqingshanite, euxenite-polycrase, fergusonite, gadolinite, huttonite, kobeite, monazite, mosandrite, samarskite, thorite,
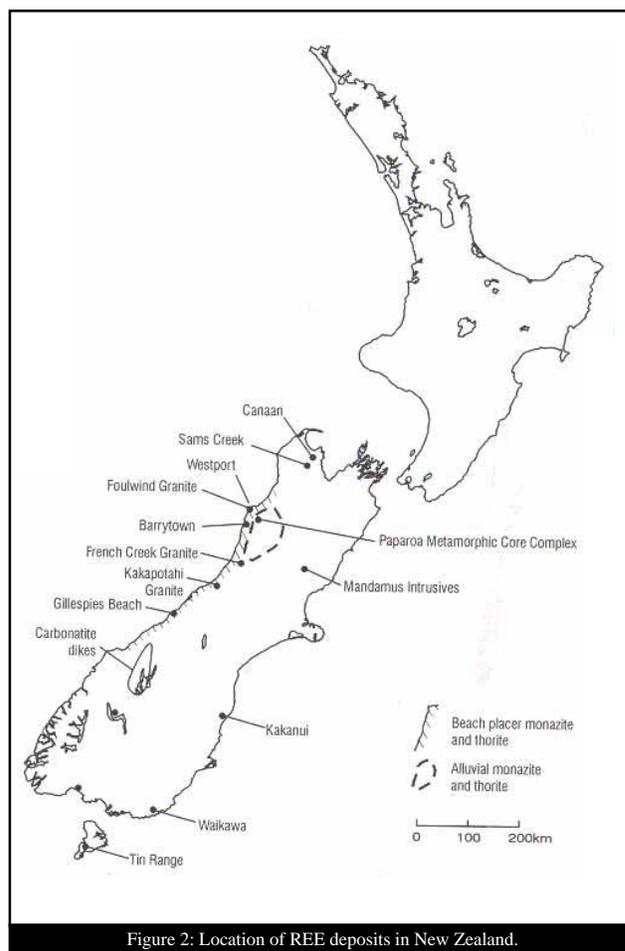
Figure 2: Location of REE deposits in New Zealand.

xenotime, and yttrotantalite (Railton and Watters, 1990). A secondary REE mineral replacing allanite in the Barrytown granite is possibly synchisite (Tulloch, unpublished data). Huttonite was discovered and first described from heavy mineral concentrates of West Coast beach sands by Pabst and Hutton (1951).

Minerals which contain minor amounts of REE include titanite, zircon, allanite and apatite, all of which are widespread in trace amounts.

Igneous and metamorphic rocks

Carbonatites
A swarm of carbonatitic lamprophyre dikes intrude Haast Schist in an area extending 110 km from the headwaters of the Paringa River on the southern side of the Alpine Fault in south Westland, south to the Shotover River in northwest Otago. Sills are also present, and a few diatreme-facies breccia pipes, similar to those exhibited by many kimberlites, have been identified (Cooper, 1986). Wallace (1975) described one of these diatreme breccia pipes located adjacent to the Alpine fault at the Moeraki River as having clasts of lherzolite and harzburgite up to 1 m in size, in a mixed matrix of 1) talc-magnesite, 2) carbonatite, and 3) minor ultramafic material. The intrusives range in size from veinlets only a few centimetres wide to a sill 85 m thick. They are late Oligocene to Early Miocene in age and consist of a magmatic series ranging in composition from ultramafic peridotite, through dominant lamprophyre to subordinate tinguaite, trachyte and carbonatite (Cooper, 1971, 1986, 1996). Fenitization of immediately adjacent country rock is widespread. Carbonatite varieties make up only a small

proportion of the intrusives. They are found in dikes and sills up to 1.2 m thick and carry accessory albite, titanian acmite, pyrite, sphalerite, galena, rutile, apatite, monazite and thorite.

Monazite occurrence in granitic and metamorphic rocks

Monazite is a common accessory mineral in many granitoid rocks of Nelson, Westland, Fiordland and Stewart Island. It is present in all of the main granitoid suites (Karamea, Rahu, Separation Point; Tulloch, 1988), but absent from Paleozoic Paringa (Cooper and Tulloch, 1992) and Triassic to Early Cretaceous Median Suites (Mortimer *et al.*, submitted). It is conspicuous in Foulwind and French Creek granites of the A-type Toropuhi Suite and French Creek Suites, respectively. Contrary to popular wisdom, monazite is not restricted to peraluminous granites, but is also found in metaluminous granodiorites and in peraluminous rocks as mafic as tonalite. The controlling factor appears to be the Ca content of the rock (Lee and Dodge, 1964) - higher Ca-granitoids generally crystallise titanite which removes REE, thereby forestalling the development of monazite. Monazite and titanite are thus generally mutually exclusive in granitoid rocks. Over the last ~5 years monazite has been used extensively for radiometric dating of igneous and metamorphic rocks, utilising both U-Pb (Tulloch *et al.*, submitted) and Th-Pb decay systems (Ireland and Gibson, 1998). Xenotime accompanies monazite in Foulwind Granite and Kakapotahi granite.

Estimated monazite contents range from 0.005 wt% in Mt Murchison Granite (Separation Point Suite) to 0.015 wt% and 0.021 wt% in core and rim respectively of the Barrytown Pluton (Karamea Suite), to 0.029 wt% and 0.042 wt% in Foulwind Granite at Cape Foulwind and Tauranga Bay, respectively. These estimates are calculated by assigning all "whole rock" Ce+La+Th to monazite only, and by assuming that these are the only REE present.

Igneous rocks with elevated REE contents

Several small areas of alkaline igneous rocks have elevated La and Ce contents. Full REE data are not available and the mineralogical hosts for these elements have not been clearly identified, except for Foulwind which contains abundant monazite and traces of xenotime. Typical values are listed in Table 6.

REE associated with the Paparoa metamorphic core complex

Hydrothermal systems formed here when hot rocks from the deep crust were rapidly uplifted and juxtaposed under brittle, water-saturated upper crustal rocks along crustal scale detachment faults. This led to the development of extensive alteration in the vicinity of these faults in the Paparoa Range (Tulloch, 1995). In addition to traces of Au, Ag, Cu, Ba, F, Fe, carbonate and U mineralisation, Tennant and Sewell (1967) reported elevated levels of REE in Paparoa Range stream sediment samples. REE abundances in Otututu and Ohikanui rivers are about four times greater than those in the Karamea area. It is interesting to note that this mineralisation in the northern Paparoa Range, with its clear relationship to major continental rifting, has much in common with the (albeit much larger and generally of Proterozoic age) Olympic Dam style of mineralisation described above.

Reference	(La+Ce+Y) ppm
Foulwind Granite, Westland Tulloch *et al.* (submitted)	286, 426
Sams Creek, Nelson Tulloch (1992)	719
Electric Granite, Fiordland Tulloch (1992)	299
French Creek Granite, Westland Tulloch *et al.* (1994)	264
Mandamus Intrusives, Canterbury Tulloch (1991)	400
Average world wide low-Ca granite Turekian and Wedepohl (1961)	187
Average world wide high-Ca granite Turekian and Wedepohl (1961)	161

Table 6: Typical REE contents of some granitic rocks.

Kakanui Mineral Breccia

The Kakanui Mineral Breccia (Deborah Volcanics Formation; Oligocene) at the Kakanui River mouth, 10 km south of Oamaru, contains dunite and eclogite nodules together with xenocrysts of pyrope garnet, augite and hornblende, a mineral assemblage resembling that of diamond-bearing kimberlite (Coombs *et al.*, 1986) and REE-bearing rocks elsewhere.

Placer deposits

Trace quantities of REE minerals such as monazite, thorite, uranothorite, and xenotime are found in the ilmenite-dominated heavy mineral fraction of sand in present-day coastal beaches of Northwest Nelson, Westland, Fiordland, Southland, at Port Pegasus on Stewart Island, and in the sand and gravel deposits along a number of rivers in Westland and Buller.

Beach deposits

REE and related minerals have been observed in heavy mineral-bearing beach sand on the West Coast during exploration for ilmenite and gold, summarised in Mineral Commodity Report 16 - Titanium (Christie and Brathwaite, 1998). The largest deposits are at Westport and Barrytown. McPherson (1978 - Table 7, Fig. 46) summarised the known distribution of monazite obtained by Grange and Bowen (1955) in the Cape Foulwind - Charleston area (Nine Mile Beach, Constant Bay, Waitakere River). Their measurements of detrital monazite concentration ranged between 0.001 and 0.02%. The monazite content of the Barrytown sand deposit was estimated at 0.12% from emission spectrographic analyses of lanthanum on 14 drill samples (Aldridge, 1970). However, estimates based on counting of monazite grains in composite drill samples, showed that the content was much lower at 0.005-0.008% (Roberts and Whitehead, 1991). Concentrations in both areas are similar to those in adjacent basement rocks (see above), indicating a local source.

At Gillespies Beach, the thorite was assayed as 76.6% thorium oxide and the uranothorite as 62.6% ThO_2 and

11.5% UO_2 (Hutton, 1950). Although no production figures are known, Nicholson (1955) estimated that during gold dredging operations, 0.1 ton of uranothorite was being recovered per week. Based on this estimate and assay figures of Hutton (1950), Caffyn (1971) estimated that 147 pounds of thorium oxide must have been produced each week. Minehan (1989) reported that thorite was present as a major mineral component in concentrate from a beach sand mining operation at Progress Valley Beach near Waikawa in Southland.

Alluvial placers

Watters (in Williams, 1959) noted that monazite had been found in stream gravels close to a granite-marble intrusive contact at Canaan, Pikikiruna Range, Northwest Nelson. Monazite "..... is conspicuous in the concentrates as rounded shot-sized grains (the largest yet found in New Zealand) which are mildly radioactive: it contains no detectable uranium but 0.5 percent thorium oxide".

Hutton (1950) reported monazite in concentrates from gold dredges working alluvial gold deposits in several localities in Westland, including Barrytown, Blackball, Snowy River, Grey River, Ngahere, Atarau, Arahura, Rimu, Kaniere and Slab Hutt. A partial analysis of monazite from the Ngahere dredge contained 1.23% U_3O_8 and 5.32% ThO_2 (Seelye in Nicholson, 1955). Nicholson calculated that 0.75 t of monazite was being discarded per week by the Ngahere Dredge. Thorite is also present in many of the concentrates, and the presence of phosphorus in analyses of some thorite from the Red Jacks, Blackball, and Snowy River dredges led Hutton (1950) to suggest the presence of xenotime mixed with the thorite. Bradley *et al.* (1979) recorded monazite, thorite and uraninite in heavy mineral concentrate from the Kaniere Dredge on the Taramakau River. Analyses of the dredge concentrate by x-ray fluorescence spectroscopy yielded thorium contents of 0.027-0.22%. Minehan (1989) noted that the Kaniere Gold Dredging Company saved several tonnes of dredge concentrates with the objective of recovering thorite from the concentrates, but no follow-up work was done.

Williams (1974) noted high concentrations of monazite in small, stream and eluvial gravel cassiterite-gold deposits on the flanks of the Tin Range, Port Pegasus, Stewart Island. These deposits were intermittently worked between 1888 and 1914 for a small quantity of gold and cassiterite.

Monazite is also present in trace quantities as detrital grains in some of the quartz conglomerate deposits of Otago (e.g. St Bathans).

About 1955, P. Corcoran found radioactive boulders near the mouth of Gout Creek close to Roaring Billy Bluff on the Haast Road (Williams, 1974). They consist of pegmatite in schist and six analyses ranged from 0.1% to 1.9% ThO_2. Similar thorite-bearing boulders were discovered in 1960 by W.F. Heinz in the Taipo Valley, 200 km to the north (Williams, 1974).

Past production, resources and future potential

There is no recorded New Zealand production of REE minerals for sale. Large ilmenite beach sand deposits near Westport, and at Barrytown north of Greymouth, contain minor amounts of monazite which could be recovered as a by-product of proposed ilmenite and gold production.

The similarities of the detachment-related mineralisation in the northern Paparoa Range to REE-bearing Olympic Dam style mineral deposits invites further investigation, as do the elevated Ce, La, Y-contents of the Mandamus Complex.

Future trends

Demand for REE is expected to increase particularly for high purity REO and metals for use in the manufacture of permanent magnets, autocatalysts and superconductors, as well as applications in corrosion resistance, heat storage and dispersal, polymerisation and in agriculture. An increased utilisation of phosphors is expected in China, as well as the increased use of yttria as an addition to zirconia and silicon nitride ceramics. There are also new applications related to environmental considerations such as in pigments for paint and plastics, substituting for heavy metal pigments (e.g. lead, chromium, cadmium and mercury); in super conductors for energy savings; in cement manufacture to reduce the temperature of calcination and help save energy; in catalytic converters for diesel engines; and in refrigeration components arising from the search for CFC replacements.

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