

Rare Earth Elements

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INTRODUCTION

The rare earth elements (REEs), which include the 15 lanthanide elements ($Z = 57$ through 71) and yttrium ($Z = 39$), are so called because most of them were originally isolated in the 18th and 19th centuries as oxides from rare minerals. Because of their reactivity, the REEs were found to be difficult to refine to pure metal. Furthermore, efficient separation processes were not developed until the 20th century because of REEs' chemical similarity. A statement attributed to Sir William Crookes, a noted English scientist, betrays the frustrations of late 19th-century chemists with this group of elements (Emsley 2001):

The 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.

All of the REEs were finally identified in the 20th century. Promethium, the rarest, was not identified until 1945, and pure lutetium metal was not refined until 1953 (Emsley 2001). Commercial markets for most of the REEs have arisen in only the past 50 years.

Most REEs are not as uncommon in nature as the name implies. Cerium, the most abundant REE (Table 1), comprises more of the earth's crust than copper or lead. Many REEs are more common than tin and molybdenum, and all but promethium are more common than silver or mercury (Taylor and McClennan 1985).

Promethium, best known as an artificial element, occurs in very minute quantities in natural materials because it has no stable or long-lived isotopes. Lanthanide elements with low atomic numbers are generally more abundant in the earth's crust than those with high atomic numbers. Those with even atomic numbers are two to seven times more abundant than adjacent lanthanides with odd atomic numbers (Table 1).

The lanthanide elements traditionally have been divided into two groups: the light rare earth elements (LREEs)—lanthanum through europium ($Z = 57$ through 63); and the heavy rare earth elements (HREEs)—gadolinium through lutetium ($Z = 64$ through 71). Although yttrium is the lightest REE, it is usually grouped with the HREEs to which it is chemically and physically similar.

The REEs are lithophile elements (elements enriched in the earth's crust) that invariably occur together naturally because all are trivalent (except for Ce^{+4} and Eu^{+2} in some environments) and have

Table 1. REEs, atomic numbers, and abundances

Element	Symbol	Atomic Number	Upper Crust Abundance, ppm*	Chondrite Abundance, ppm†
Yttrium	Y	39	22	na‡
Lanthanum	La	57	30	0.34
Cerium	Ce	58	64	0.91
Praseodymium	Pr	59	7.1	0.121
Neodymium	Nd	60	26	0.64
Promethium	Pm	61	na	na
Samarium	Sm	62	4.5	0.195
Europium	Eu	63	0.88	0.073
Gadolinium	Gd	64	3.8	0.26
Terbium	Tb	65	0.64	0.047
Dysprosium	Dy	66	3.5	0.30
Holmium	Ho	67	0.80	0.078
Erbium	Er	68	2.3	0.20
Thulium	Tm	69	0.33	0.032
Ytterbium	Yb	70	2.2	0.22
Lutetium	Lu	71	0.32	0.034

* Source: Taylor and McClennan 1985

† Source: Wakita, Rey, and Schmitt 1971.

‡ na = not available.

similar ionic radii. An increase in atomic number in the lanthanide group is not accompanied by change in valence, and the lanthanide elements all inhabit the same cell in most versions of the periodic table. The similar radii and oxidation states of the REEs allow for liberal substitution of the REEs for each other into various crystal lattices. This substitution accounts for their wide dispersion in the earth's crust and the characteristic multiple occurrences of REEs within a single mineral. The chemical and physical differences that exist within the REEs group are caused by small differences in ionic radius and generally result in segregation of REEs into deposits enriched in either light lanthanides or heavy lanthanides plus yttrium.

The relative abundance of individual lanthanide elements has been found useful in the understanding of magmatic processes and natural aqueous systems. Comparisons are generally made using a

logarithmic plot of lanthanide abundances normalized to abundances in chondritic (stony) meteorites. The use of this method eliminates the abundance variation between lanthanides of odd and even atomic number, and allows determination of the extent of fractionation between the lanthanides, because such fractionation is not considered to have taken place during chondrite formation. The method also is useful because chondrites are thought to be compositionally similar to the original earth's mantle. Europium (Eu) anomalies (positive or negative departures of europium from chondrite-normalized plots) have been found to be particularly effective for petrogenetic modeling. In addition, REE isotopes, particularly of neodymium and samarium, have found use in petrogenetic modeling and geochronology.

HISTORY OF REE PRODUCTION

REEs were originally produced in minor amounts from small deposits in granitic pegmatite, the geologic environment in which they were first discovered. During the second half of the 19th century and the first half of the 20th century, REEs came mainly from placer deposits, particularly those of the southeastern United States. With the exception of the most abundant lanthanide elements (cerium, lanthanum, and neodymium), individual REEs were not commercially available until the 1940s. Between 1965 and 1985, most of the world's REEs came from Mountain Pass, California. Heavy mineral sands from placers in many parts of the world, however, were also sources of by-product REE minerals, and Australia was a major producer from such sources until the early 1990s. Until recently, Russia also was an important REE producer from a hard rock source. During the 1980s, China emerged as a major producer of REE raw materials, while the Australian and American market shares decreased dramatically (Figure 1). Since 1998, more than 80% of the world's REE raw materials have come from China, and most of this production is from the Bayan Obo deposit in Inner Mongolia. Table 2 gives recent annual production figures by country, and Figure 2 shows locations of currently and recently productive REE mines.

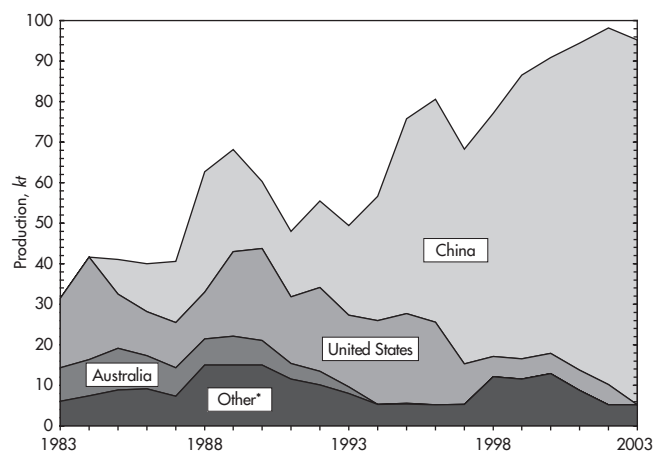
MINERALS THAT CONTAIN REES

Although REEs comprise significant amounts of many minerals, almost all production has come from less than 10 minerals. Table 3 lists those that have yielded REEs commercially or have potential for production in the future. Extraction from a potentially economic REE resource is strongly dependant on its REE mineralogy. In the past, producing deposits were limited to those containing REE-bearing minerals that are relatively easy to concentrate because of coarse grain size or other attributes. Minerals that are easily broken down, such as the carbonate bastnasite, are more desirable than those that are difficult to dissociate, such as the silicate allanite. Placer monazite, once an important source of REEs, has been largely abandoned because of its high thorium content. Recently, REEs absorbed on clay minerals in laterite have become important sources of REEs in China. For more information on REE-bearing minerals, see works by Mariano (1989a); and Jones, Wall, and Williams (1996).

GEOLOGY OF REE DEPOSITS

Iron-REE Deposits

Some iron deposits contain REE resources, and such deposits have been exploited in only one area—Bayan Obo, China. These deposits constitute the largest known REE resource in the world (Table 4) and are now the most important REE source in the world (Haxel, Hedrick, and Orris 2002).



*"Other" includes India, Brazil, Kyrgyzstan, Sri Lanka, Russia, Malaysia, and Thailand.

Figure 1. Production of REEs by China, the United States, Australia, and other countries, 1983–2003

Iron-LREE-niobium deposits at Bayan Obo in Inner Mongolia, China, were discovered by Russian geologists in 1927 (Argall 1980) when Inner Mongolia was under the control of the former U.S.S.R. REEs are recovered from iron-REE-niobium (Fe-REE-Nb) ore bodies that have been mined from more than 20 sites since mining started in 1957 (Drew, Meng, and Sun 1990). The two largest are the Main and East ore bodies (Figure 3), each of which include iron-REE resources with more than 1,000 m of strike length and average 5.41% and 5.18% rare earth oxides (REOs), respectively (Yuan et al. 1992). Total reserves have been reported as at least 1.5 billion t of iron (average grade 35%), at least 48 Mt of REOs (average grade 6%), and about 1 Mt of niobium (average grade 0.13%) (Drew, Meng, and Sun 1990). The REE ore consists of three major types: REE-iron ore, the most important type; REE ore in silicate rock; and REE ore in dolomite (Yuan et al. 1992). Massive REE-iron ore occurs in 100-m-thick lenses with local banded and breccia structures. Banded and streaky fluorite-rich REE-iron ore has the highest REE content, locally more than 10% REOs. Major oxide chemistries of several Bayan Obo ore types are shown in Table 5. REEs are mainly in bastnasite and monazite, but at least 20 other REE-bearing minerals have been identified (Yuan et al. 1992). Bayan Obo ore has extreme LREE enrichment with no europium anomalies (Figure 4) and low strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) (Nakai et al. 1989; Philpotts et al. 1989). Alkali-rich alteration (fentonization), predominated by sodic amphibole and potash feldspar, is associated with the REE mineralization (Drew, Meng, and Sun 1990).

The Bayan Obo ore is hosted by dolomite of the Bayan Obo Group, a Middle Proterozoic clastic and carbonate sedimentary sequence (Qiu, Wang, and Zhao 1983; Chao et al. 1997) that occurs in an 18-km-long syncline (Drew, Meng, and Sun 1990). The Bayan Obo Group was deposited unconformably on 2.35-Ga migmatites, and, along with Carboniferous volcanics, was deformed during a Permian continent-to-continent collision event dominated by folding and thrusting (Drew, Meng, and Sun 1990). Intrusion of large amounts of Permian granitoid rocks also resulted from this collision.

The age of the REE mineralization is a matter of debate. It has been dated at 1600 Ma (Yuan et al. 1992) and 550 to 400 Ma (Chao et al. 1997). Most researchers agree that Fe-REE-Nb mineralization at Bayan Obo took place over a long period of time.

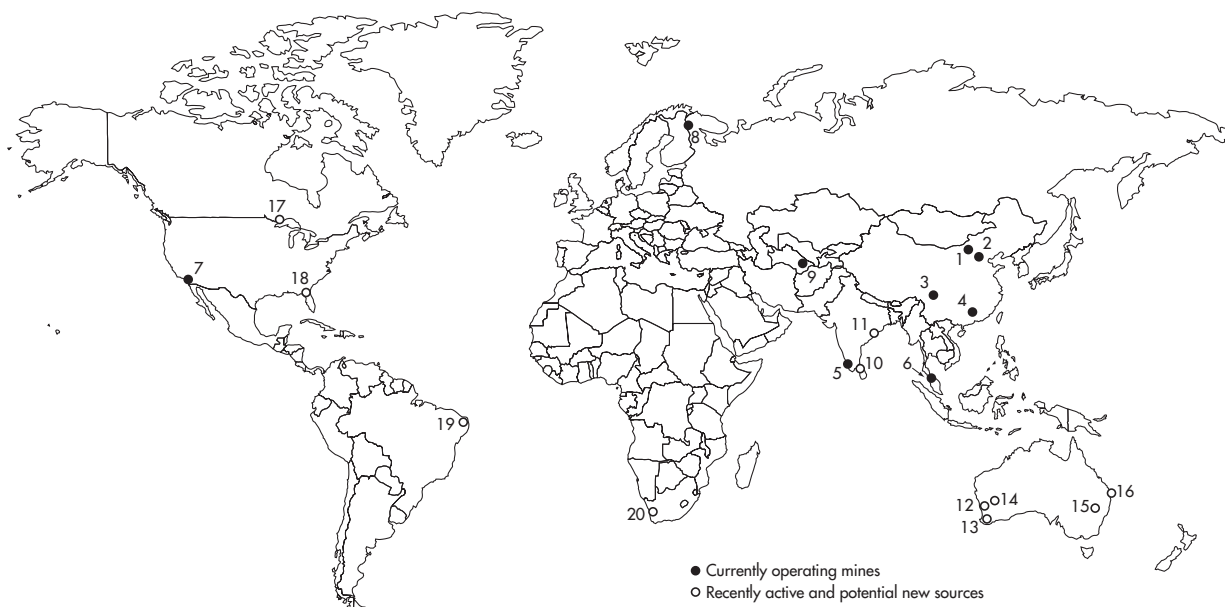
Table 2. Estimated annual world mine production of REEs, by country

Country	1983	1985	1987	1989	1991	1993	1995	1997	1999	2001	2003*
Metric Tons of REO Equivalent											
Australia	8,328	10,304	7,047	7,150	3,850	1,650	110	0	0	0	0
Brazil	2,891	2,174	2,383	1,377	719	270	103	0	0	0	0
China	na†	8,500	15,100	25,220	16,150	22,100	48,000	53,000	70,000	80,600	90,000
India	2,200	2,200	2,200	2,365	2,200	2,500	2,750	2,750	2,700	2,700	2,700
Kyrgyzstan	na	na	na	696	721	0	na	na	6,115	3,800	na
Malaysia	601	3,869	1,618	1,700	1,093	224	452	422	631	281	450
Mozambique	2	2	0	0	0	0	0	0	0	0	0
South Africa	0	0	660	660	237	237	0	0	0	0	0
Sri Lanka	165	110	110	110	110	110	110	110	120	0	0
Thailand	164	459	270	368	229	127	0	7	0	0	0
Russia	na	na	na	7,626	6,138	4,468	2,000	2,000	2,000	2,000	2,000
United States	17,083	13,428	11,100	20,787	16,465	17,754	22,200	10,000	5,000	5,000	0
Zaire	6	0	53	96	66	11	5	0	0	0	0
Total	31,439	41,047	40,541	68,155	47,978	49,449	75,730	68,288	86,566	94,381	95,150

Courtesy of USGS.

* Estimated. Some data have been added or modified using unpublished data from USGS files.

† na = not available.



Location No.	Location Name	Deposit Type	Location No.	Location Name	Deposit Type
1	Bayan Obo, China	Fe-REE-Nb deposit	11	Orissa, India	Monazite by-product, coastal placers
2	Weishan, China	Bastnasite-barite veins	12	Eneabba, Australia	Monazite by-product, coastal placers
3	Maoniuping, China	Bastnasite-barite veins	13	Capel and Yoganup, Australia	Monazite by-product, coastal placers
4	Xunwu and Longnan, China	Lateritic clay	14	Mount Weld, Australia	Lateritized carbonatite
5	Chavara, India	Monazite by-product, coastal placers	15	Dubbo, Australia	Altered alkaline complex
6	Perak, Malaysia	Xenotime by-product, tin placers	16	North Stradbroke Island, Australia	Monazite by-product, coastal placers
7	Mountain Pass, USA	Bastnasite-barite carbonatite	17	Elliot Lake, Canada	Uraniferous conglomerate
8	Lovozero, Russia	Loparite in peralkaline complex	18	Green Cove Springs, USA	Monazite by-product, placer
9	Aktys, Kyrgyzstan	Polymetallic deposit	19	Camaratuba, Brazil	Monazite by-product, coastal placers
10	Northern Sri Lanka	Monazite by-product, coastal placers	20	Steenkampskraal, South Africa	Monazite-apatite vein

Figure 2. Locations of the world's rare earth mines

Table 3. Minerals that contain REEs and occur in economic or potentially economic deposits

Mineral	Formula*	REO wt % ^{†‡}
Aeschynite	(Ln,Ca,Fe,Th)(Ti,Nb) ₂ (O,OH) ₆	36
Allanite (orthite)	(Ca,Ln) ₂ (Al,Fe) ₃ (SiO ₄) ₃ (OH)	30
Anatase	TiO ₂	3
Ancylite	SrLn(CO ₃) ₂ (OH)•H ₂ O	46
Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	19
Bastnasite	LnCO ₃ F	76
Brannerite	(U,Ca,Ln)(Ti,Fe) ₂ O ₆	6
Britholite	(Ln,Ca) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)	62
Cerianite	(Ce,Th)O ₂	81 [§]
Cheralite	(Ln,Ca,Th)(P,Si)O ₄	5
Churchite	YPO ₄ •2H ₂ O	44 [‡]
Eudialyte	Na ₁₅ Ca ₆ (Fe,Mn) ₃ Zr ₃ (Si,Nb)Si ₂₅ O ₇₃ (OH,Cl,H ₂ O) ₅	10
Euxenite	(Ln,Ca,U,Th)(Nb,Ta,Ti) ₂ O ₆	<40 [§]
Fergusonite	Ln(Nb,Ti)O ₄	47
Florencite	LnAl ₃ (PO ₄) ₂ (OH) ₆	32 [§]
Gadolinite	LnFeBe ₂ Si ₂ O ₁₀	52
Huanghoite	BaLn(CO ₃) ₂ F	38
Hydroxylbastnasite	LnCO ₃ (OH,F)	75
Kainosite	Ca ₂ (Y,Ln) ₂ Si ₄ O ₁₂ CO ₃ •H ₂ O	38
Loparite	(Ln,Na,Ca)(Ti,Nb)O ₃	36
Monazite	(Ln,Th)PO ₄	71
Mosandrite	(Ca,Na,Ln) ₁₂ (Ti,Zr) ₂ Si ₇ O ₃₁ H ₆ F ₄	<65 [§]
Parisite	CaLn ₂ (CO ₃) ₃ F ₂	64
Samarskite	(Ln,U,Fe) ₃ (Nb,Ta,Ti) ₅ O ₁₆	12
Synchisite	CaLn(CO ₃) ₂ F	51
Thalenite	Y ₃ Si ₃ O ₁₀ (OH)	63 [§]
Xenotime	YPO ₄	61 [§]
Yttrotantalite	(Y,U,Fe)(Ta,Nb)O ₄	<24 [§]

* Source for mineral formulas: Mandarino 1999, with Ln = lanthanide elements.

† Sources for REO content: Frondel 1958; Overstreet 1967; Anon. 1980; Kapustin 1980; Mazzi and Munno 1983; Mariano 1989a.

‡ Where more than one analysis is available, the analysis with the highest REO content is reported (e.g., REO for monazite from the Mountain Pass carbonatite is reported; monazite from pegmatites and metamorphic rocks generally has lower REO).

§ Stoichiometric calculation of REO content.

Recent research points to ore formation during hydrothermal replacement of sedimentary dolomite, possibly related to one of the following:

- Alkaline or carbonatite magmatism (Drew, Meng, and Sun 1990; Campbell and Henderson 1997; Smith and Henderson 2000; Smith, Henderson, and Campbell 2000)
- Original emplacement of both the host dolomite and ore as igneous carbonatite with subsequent tectonic deformation (Le Bas, Spiro, and Yang 1997)
- Formation of host and ore by marine exhalation of alkalic or carbonatite-related fluids

Whatever its origin, the Bayan Obo deposits now dominate worldwide REE production and probably will do so for many years to come.

The Pea Ridge iron deposit in Missouri contains an unexploited high-grade REE resource of unknown but probably small size in breccia pipes associated with 1.48-Ga granite and syenite (Kisvarsanyi, Sims, and Kisvarsanyi 1989). Bulk samples of REE-rich breccia, which contain monazite and xenotime, average about 12% REEs (Nuelle et al. 1992). Although the Pea Ridge resource is LREE-dominated, it also contains significant HREEs.

Mill tailings from processing magnetite deposits in Precambrian gabbro and syenite at Mineville, New York, are an REE resource of unknown size. They contain apatite that averages more than 11% REOs, including about 2% Y₂O₃ (McKeown and Klemic 1956).

The important magnetite and hematite deposits at Kiruna, Sweden, average 0.7% and 0.5% REOs, respectively, and other Swedish iron deposits contain similar amounts of REOs (Parak 1973). The REEs in these deposits are reportedly in apatite and monazite.

The huge Middle Proterozoic Olympic Dam copper-uranium-silver-gold deposit, South Australia, may also be included in this deposit type because most of the ore is breccia that contains 40% to 90% hematite along with quartz, sericite, fluorite, barite, sulfides, and REE minerals (Oreskes and Einaudi 1990). Olympic Dam is a potential source of by-product REEs, but typical content is about 0.5% total REEs, and there are no plans for REE production from the deposit. Extremely fine-grained monazite and bastnasite are the most abundant REE minerals, and the LREE/HREE ratio is high in Olympic Dam ore.

Carbonatite Deposits

Many carbonatite intrusions are enriched in REEs; Orris and Grauch (2002) list more than 100 carbonatite occurrences that contain REE minerals. Brief descriptions of REE mineral occurrences in carbonatites worldwide may be found in works by Mariano (1989a), Woolley (1987), and Wall and Mariano (1996).

Despite the abundance of REE-bearing carbonatites, REEs have been produced from only one, the Mountain Pass deposit in California. Although the Mountain Pass mine and plant did not operate in 2003, REE products were shipped from stockpile (Hedrick 2004a). Beginning in 1954, the Mountain Pass deposit was mined exclusively for REEs by Molycorp, Inc. (originally Molybdenum Corp. of America and now a subsidiary of Unocal). In 1987, proven and probable reserves totaled 29 Mt with an average grade of 8.9% REOs based on a 5% cutoff grade (Castor 1991). Current reserves are in excess of 20 Mt of ore at similar grade (Castor and Nason 2004). The ore typically contains 10% to 15% bastnasite, 65% calcite or dolomite, and 20% to 25% barite. Other gangue minerals, such as strontianite and talc, are present in significant amounts locally. Galena is locally abundant, but other sulfide minerals are rare. Bastnasite is the only mineral processed, although nine other REE minerals occur at Mountain Pass (Castor and Nason 2004). Mountain Pass ore has high LREEs and HREEs (Figure 4). The major oxide chemistry of Mountain Pass REE ore types is shown in Table 5.

The Mountain Pass carbonatite, which has been dated at about 1.4 Ga (DeWitt, Kwak, and Zartman 1987), is a moderately dipping, tabular intrusion (Figure 5) into granulite-grade gneiss. It is associated with ultrapotassic alkaline plutons of similar age, size, and orientation, as well as with abundant carbonatite and alkaline dikes, and is in a narrow north-trending zone of ultrapotassic alkaline igneous rocks at least 130 km long (Castor 1991; Castor and Nason 2004).

Elsewhere in the western United States, carbonatites have been investigated as possible sources of REEs, but none rival the Mountain Pass deposit as a REE resource. Similar to the Mountain

Table 4. Size and grade of some productive and potentially productive REE deposits

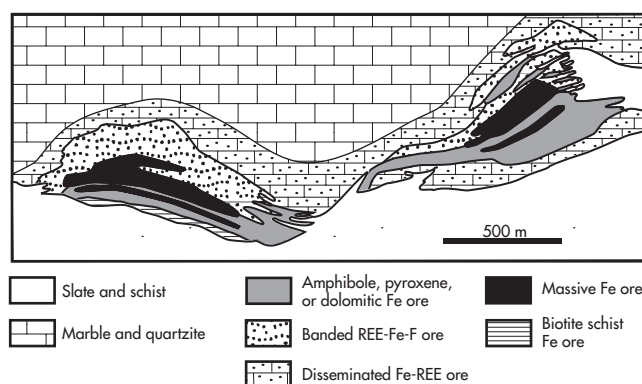
Deposit or District	Country	Size, t REO	Grade, % REO	Deposit Type	Recent Production	Reference
Bayan Obo	China	48,000,000	6	Iron-rich	Yes	Drew, Meng, and Sun 1990
Araxá	Brazil	8,100,000	1.8	Carbonatite laterite	No	Morteani and Preinfalk 1996
Mountain Pass	United States	1,800,000	8.9	Carbonatite	Yes	Castor and Nason 2004
Mount Weld	Australia	1,700,000	11.2	Carbonatite laterite	No	Mariano 1989b
Dubbo	Australia	700,000	0.86	Trachyte	No	Australian Zirconia Ltd. 2000
Mrima Hill	Kenya	300,000	5	Carbonatite laterite	No	Orris and Grauch 2002
Nolan's Bore	Australia	150,000	4	Vein	No	Anon. 2003
Xunwu and Longnan	China	Unknown	0.05–0.2	Laterite	Yes	Wu, Yuan, and Bai 1996
Lovozero	Russia	Unknown	0.01	Peralkaline syenite	Yes	Hedrick, Sinha, and Kosynkin 1997
Maoniuping	China	Unknown	2	Vein	Yes	Wu, Yuan, and Bai 1996
Weishan	China	Unknown	1.6	Vein	Yes	Wu, Yuan, and Bai 1996
Aktyus	Kyrgyzstan	Unknown	0.25	Unknown	Yes	Geological Survey of Kyrgyzstan 2004
Eneabba	Australia	Unknown	0.001	Placer	Yes	Griffiths 1984

Pass carbonatite, most have high LREE/HREE ratios. The large Cambrian Iron Hill carbonatite in the Powderhorn District of Colorado has been considered a possible source of REEs, but Armbrustmacher (1980) reported a grade of about 0.5% REEs. Carbonatite dikes in the Powderhorn District that contain up to 3% REOs constitute a resource of unknown size (Olson and Hedlund 1981), and dikes in the nearby Wet Mountains constitute a small resource with a grade of about 2.5% REOs (Armbrustmacher 1988). Phanerozoic carbonatite dikes that contain as much as 21% REOs (Crowley 1960), mainly in monazite, allanite, and ancylite (Heinrich and Levinson 1961), are present in the North Fork Area on the Idaho–Montana border, but the size of this resource is probably small because dikes with high REO contents are generally less than 1 m thick.

Carbonatite complexes in eastern Canada also contain REE mineralization. A britholite-bearing carbonatite dike in Mesozoic carbonatite at Oka, Quebec, is an REE resource of unknown size and grade (Mariano 1989a). Bastnasite and monazite zones containing up to 4.5% LREEs have been identified in the Late Proterozoic St-Honore Complex in Quebec, with one 80-m drill intercept averaging more than 3% REOs (Vallee and Dubuc 1970).

Brazilian carbonatites contain significant REE resources but have yielded only minor production to date. Niobium ore in the Barreiro Complex at Araxá, Minas Gerais, which comprises 450+ Mt averaging 2.5% Nb₂O₅, contains about 4.4% REOs (Issa Filho, Lima, and Souza 1984).

African carbonatites also contain LREE-dominated deposits that are largely unexploited. Kangankunde Hill, Malawi, is underlain by carbonatite dikes in which the main REE phase is monazite that is almost thorium-free (Garson 1966). The dikes are thought to contain a resource of several hundred thousand tons of monazite at an average grade of more than 5% (Deans 1966). Mariano (1989a) suggested that monazite in Kangankunde Hill carbonatite is of primary igneous origin like the bastnasite at Mountain Pass, but subsequent work indicated that the monazite, as well as associated bastnasite and florencite-goyazite, was formed from an original REE phase during hydrothermal activity (Wall and Mariano 1996). Carbonatite dikes at Wigu Hill, Tanzania, contain up to 20% REOs as monazite and REE fluorocarbonate minerals of possible hydrothermal origin (Deans 1966). The Palabora carbonatite in South Africa, which occurs in a large Early Proterozoic potassic alkaline complex, has significant copper and apatite production and has been evaluated as a source of REEs. Potential by-product from apatite



Adapted from Chao et al. 1997.

Figure 3. Geologic map of the Main and East iron-REE-niobium ore bodies at Bayan Obo, China

concentrates that contain 0.4% to 0.9% REOs has been estimated at 4,250 tpy (Notholt, Highley, and Deans 1990).

Sill-like lenses of bastnasite-fluorite-barite rock as much as 30 m thick with about 5% REEs are associated with carbonatite at Kizilçaören, Turkey (Hatzl et al. 1990). The carbonatite occurs in dikes associated with intrusive Tertiary phonolites and trachytes along with alkaline pyroclastic rocks. The unexploited Kizilçaören resource is dominantly LREEs (G. Morteani, personal communication).

Lateritic Deposits

Lateritic deposits that occur over low-grade primary sources, such as carbonatites and syenites, have been studied as potential REE sources since the 1980s. Such deposits may constitute large resources and some have high REE contents; however, only two deposits in China have been exploited to date.

REEs have been produced in increasing quantities in recent years from surficial clay deposits in southern China, and Orris and Grauch (2002) list 18 Chinese occurrences of such material. In 1992, REEs from these deposits comprised 14% of Chinese production (Wu, Yuan, and Bai 1996), and this source has had a strong impact on yttrium supplies since 1988. The deposits reportedly form weathering crusts over granite (Ren 1985; Wu,

Table 5. Major oxide chemistry of ore samples from Bayan Obo and Mountain Pass

Samples	Bayan Obo*					Mountain Pass†					
	Mfe	Ffe	AeFe	RiFe	MDT	7B30-20	7B30-45A	7B30-28B	7B31-10	85-4	R-724
SiO ₂	4.81	2.18	23.86	10.79	8.74	na‡	na	na	na	0.40	1.63
TiO ₂	0.27	0.62	0.56	0.55	0.28	1.00	0.15	0.23	0.08	0.01	0.01
Al ₂ O ₃	0.22	0.66	1.55	0.83	0.74	0.06	0.25	0.17	0.26	0.01	0.01
Fe ₂ O ₃ §	74.73	39.29	31.61	44.59	11.69	7.72	13.87	37.17	5.00	0.24	1.77
MnO	0.79	0.12	0.07	5.95	1.18	0.01	0.03	0.02	0.01	0.24	0.45
MgO	0.99	0.31	0.30	3.52	13.23	<0.03	0.07	0.25	0.12	0.04	6.41
CaO	8.78	26.26	11.59	16.15	27.09	27.98	27.98	3.92	8.67	21.30	11.73
SrO	0.36	3.90	5.67	1.15	0.25	0.05	0.10	0.07	0.09	14.15	2.49
BaO	na	na	na	na	na	0.04	3.80	2.79	2.46	14.63	25.12
Na ₂ O	0.25	0.25	4.06	0.62	0.12	na	na	na	na	0.05	0.07
K ₂ O	0.09	0.08	0.57	0.92	0.58	<0.24	<0.24	<0.24	<0.24	0.05	0.09
P ₂ O ₅	0.94	2.71	2.85	1.16	1.47	na	na	na	na	0.04	0.29
F	5.89	16.83	7.25	8.31	1.83	17.00	14.4	1.68	4.49	0.70	1.40
CO ₂	na	na	na	na	na	na	na	na	na	19.84	18.26
SO ₃	na	na	na	na	na	na	na	na	na	18.26	15.43
LOI	2.89	5.15	5.62	5.60	25.23	na	na	na	na	na	na
RE ₂ O ₃	2.73	9.49	7.72	3.24	3.98	19.32	8.67	10.89	42.75	9.89	13.18
Nb ₂ O ₅	na	na	na	na	na	0.36	0.02	0.05	0.53	0.001	0.004
Total	103.74	107.85	103.28	103.38	96.41	73.54	69.34	57.24	64.46	99.85	98.34

Source: Yuan et al 1992; Chao et al. 1997; Castor and Nason 2004.

* Bayan Obo:

Mfe = massive REE-Fe ore

Ffe = fluorite REE-Fe ore

AeFe = aegerine REE-Fe ore

RiFe = riebeckite REE-Fe ore

MDT = magnetite-dolomite ore

7B30-20 = high-REE, low-Fe banded ore

7B30-45A = bastnasite-apatite-pyroxene-fluorite ore

7B30-28B = high-Fe, REEs, and fluorite ore

7B31-10 = high-REE, low-Fe, and low-F ore

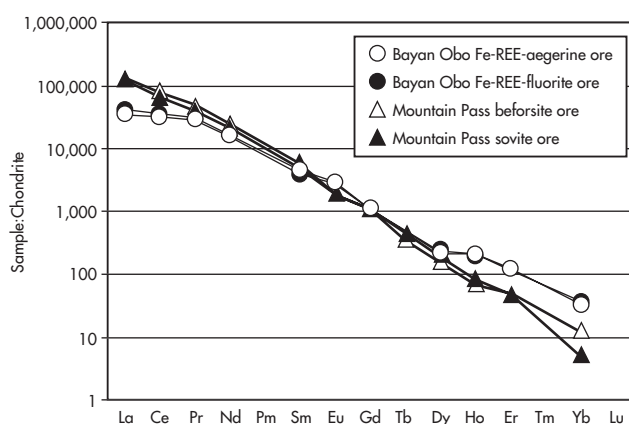
† Mountain Pass:

85-4 = bastnasite-barite sovite, Sulphide Queen ore body

R-724 = bastnasite-barite beforite, Sulphide Queen ore body.

‡ na = not available.

§ All Fe as Fe₂O₃.



NOTE: REE data not normalized to 100% prior to chondrite normalization.

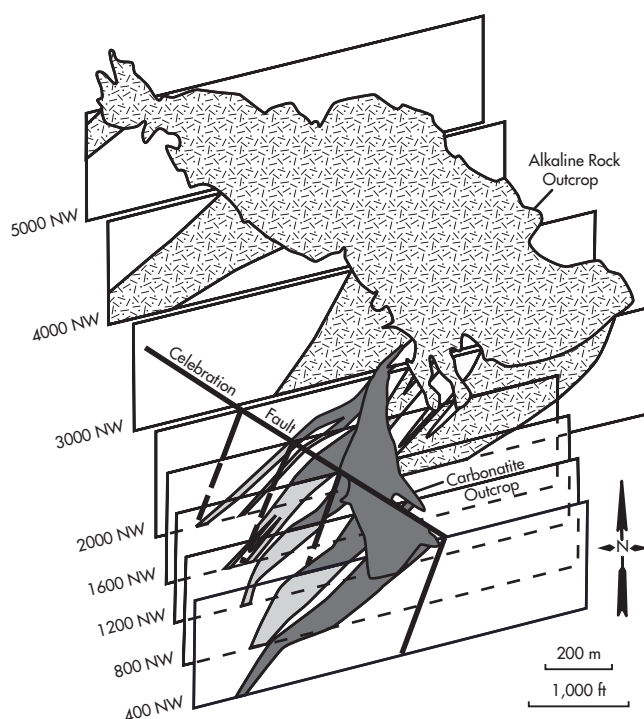
Figure 4. Chondrite-normalized plot of REEs in ores from Bayan Obo, China, and Mountain Pass, United States (data sources: Castor 1986; Yuan et al. 1992)

Yuan, and Bai 1996). The ore, referred to as REE-bearing ionic absorption clay, mostly comes from two sites in Jiangxi Province—Longnan and Xunwu, the former yielding HREE- and yttrium-rich material and the other, LREE-rich material (O'Driscoll 2003). Ore from Longnan has an HREE-dominated

distribution pattern very similar to that of xenotime, whereas ore from Xunwu is relatively enriched in lanthanum (Hedrick 1992; Figure 6). Both ores have relatively low cerium content, suggesting deposition from REE-bearing groundwater with depleted cerium that results from the element's insolubility in the oxidized (Ce⁴⁺) state. The ore bodies are 3 to 10 m thick and occur mainly in a wholly weathered zone composed of halloysite and kaolinite with residual quartz and feldspar; grades are reported at 0.05% to 0.2% REOs (Wu, Yuan, and Bai 1996). The deposits are considered to be laterites and show similarities to a number of other lateritic deposits formed over alkaline igneous rocks and carbonatite (Morteani and Preinfalk 1996).

REE-enriched lateritic material overlying carbonatite is present in many sites worldwide, mostly in the tropics. Orris and Grauch (2002) list more than 50 such occurrences, but, other than the Chinese deposits, none have produced significant amounts of REEs.

The Mount Weld REE deposit in southern Western Australia is in the laterized cap over a large carbonatite (Figure 7) dated at 2.0 Ga (Duncan and Willett 1990). Although LREE/HREE ratios are generally high, the laterite is locally enriched in HREEs and yttrium. Published reserve figures are 15.4 Mt with 11.2% REOs + Y₂O₃ (Mariano 1989a), and 2.3 Mt with 18.0% REOs (Willis 2002). Large volumes of ore contain an average of 0.33% Y₂O₃, and niobium and tantalum enrichment has also been reported (O'Driscoll 1988). Data from Lottermoser (1990) indicate that unweathered carbonatite at depth contains 0.1% to 0.2% REOs. REE enrichment at Mount Weld is thought to have been caused by



Adapted from W. Buckovic, personal communication.

Figure 5. Stacked cross sections through the Mountain Pass REE carbonatite ore body (gray) and a major associated alkaline rock mass (patterned)

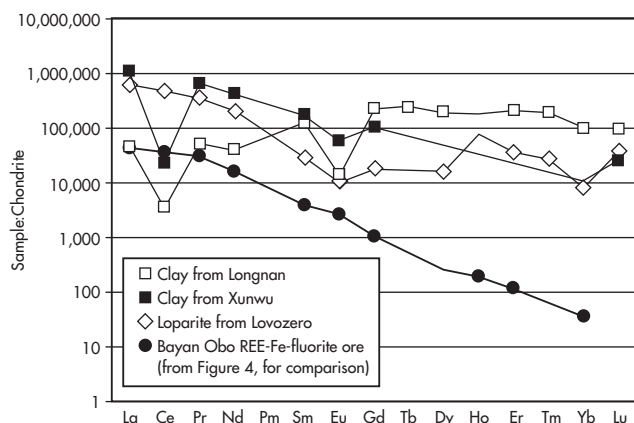
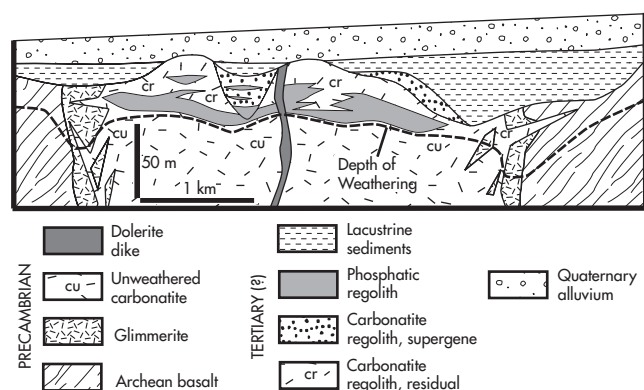


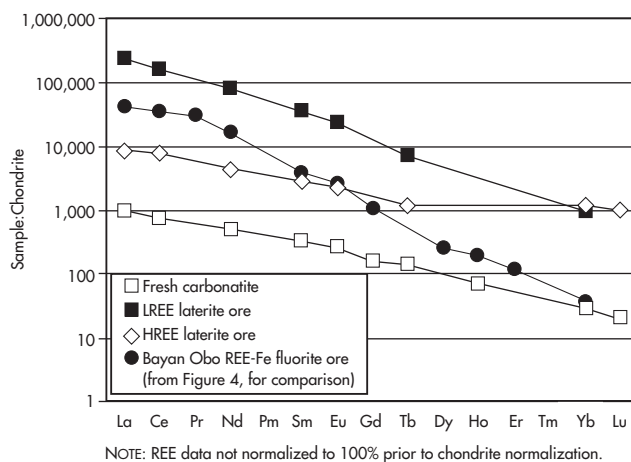
Figure 6. Chondrite-normalized plot of REE distribution (normalized to 100%) in ion absorption clay ores from China and loparite from Russia (data source: Hedrick 1992)

long-term leaching and redeposition by groundwater; it mainly consists of REE phosphates (Mariano 1989a), including the yttrium-rich mineral churchite (Lottermoser 1988). During the formation of the weathered profile since Permian glaciation, LREEs were incorporated in phosphate and alumino-phosphate minerals in the upper part of the profile, and HREEs and Y were deposited as churchite at lower levels (Lottermoser 1990), leading to the formation of both LREE- and HREE-enriched ore (Figure 8). The Yangibana REE



Adapted from Duncan and Willett 1990.

Figure 7. East-west geological cross section through the Mount Weld carbonatite and its weathered cap



NOTE: REE data not normalized to 100% prior to chondrite normalization.

Figure 8. Chondrite-normalized plot of REEs in laterite and carbonatite from Mount Weld, Australia (data source: Lottermoser 1990)

prospect in northern Western Australia, a gossan containing as much as 11% REOs (O'Driscoll 1988), is thought to have been formed by weathering from a carbonatite associated with Early Proterozoic alkaline rocks.

The Araxá carbonatite complex in Brazil contains 800,000 t of supergene-enriched laterite that averages 13.5% REOs, mainly in the phosphate minerals gorceixite and goyazite (Mariano 1989a). In the Catalão I Complex about 300 km southeast of Araxá, phosphatic laterite comprises a resource of about 2 Mt averaging 12% REOs. The REEs are mainly in secondary phosphate minerals, such as gorceixite (Mariano 1989a; Morteani and Preinfalk 1996). Laterized carbonatite in the Maicuru Complex, Pará, northern Brazil, contains phosphatic material with as much as 17% REEs (Costa et al. 1991). Cerro Impacto, a large circular structure thought to be a deeply weathered carbonatite that is located in the Amazon region of Venezuela, contains as much as 11% REEs in thick laterite (O'Driscoll 1988).

Deeply weathered Brazilian carbonatites that contain large titanium resources in the form of anatase with associated REE phosphate minerals are also a potential source of by-product REEs

with high LREE/HREE ratios (Mariano 1989a). Titanium concentrates from a pilot plant contain more than 3% REEs that must be removed to produce commercial titania. Reserves are known to be substantial; the largest deposit, at Serra Negra, Minas Gerais, contains 200 Mt averaging 27.7% TiO₂ (Anon. 1984). Other poorly explored carbonatites in the Amazon region of South America are known to host supergene REE mineralization (Mariano 1989b).

REE-enriched laterites occur at 17 sites in Africa (Orris and Grauch 2002). The most thoroughly investigated deposit is probably monazite-rich laterite that includes 6 Mt of material with about 5% REOs that overlies carbonatite at Mrima Hill, Kenya. REE enrichment in the form of secondary hydroxylbastnasite and other minerals has been reported in karst-related lateritic deposits in Europe, such as upper Jurassic bauxite deposits in Montenegro (Maksimović and Pantó 1996).

Placer Deposits

Most placer accumulations with significant amounts of REE minerals are Tertiary or Quaternary deposits derived from source areas that include granitic rocks or high-grade metamorphic rocks; however, paleoplacer deposits that are as old as Precambrian contain REE resources. Orris and Grauch (2002) list more than 360 REE-bearing placers. Most commercial deposits are in sands of marine origin along or near present coastlines and consist of titanium mineral placers with by-product zircon and monazite; some contain xenotime. In the 1980s, monazite and xenotime from titania-zircon paleobeach placers in Australia were the third most important source of REEs in the world, but Australia currently exports little or no REE minerals from such sources, owing to their high thorium content.

Placer rutile-zircon-ilmenite deposits at Eneabba on Australia's west coast north of Perth, which produced about 2,500 t of monazite annually, were brought into production in the late 1970s. These deposits are still productive, but little or no monazite is currently marketed from them. Heavy minerals comprise about 6% of the sand mined at Eneabba, and monazite makes up 0.5% to 7.0% of the heavy minerals (Shepherd 1990). The heavy mineral sands lie 30 m or more above present sea level and were deposited in late Tertiary or early Pleistocene time (Lissiman and Oxenford 1975). Archean metamorphic rocks in the interior provided heavy minerals to Mesozoic sedimentary rocks that were reworked to form the deposits. In the Geographe Bay area near Capel, ilmenite-zircon paleobeach deposits that have been mined since the mid-1950s occur along a strike length of about 50 km in Pleistocene to Recent sands (Welch, Sofoulis, and Fitzgerald 1975). The setting and source are similar to those described for Eneabba. Although the average heavy mineral grade of Geographe Bay deposits is somewhat higher than at Eneabba, the monazite content of heavy mineral concentrates is lower, at 0.04% to 1.1% (Welch, Sofoulis, and Fitzgerald 1975).

Minor amounts of monazite were once produced from placers along Australia's east coast. Rutile and zircon are the main mineral products from these operations, which exploit Quaternary beach placers and sand dunes. Heavy mineral content in some of the deposits is less than 0.5% (Griffiths 1984), and monazite comprises less than 1% of the heavy mineral concentrate (McKellar 1975). The WIM 150 deposit, a placer in an interior basin in Victoria, contains large REE mineral resources. A 14-m-thick titanium and zirconium mineral sand deposit, it underlies an extensive area amenable to dredging. Estimated REE mineral reserves exceed 580,000 t monazite and 170,000 t xenotime (O'Driscoll 1988).

In addition to Australia, by-product monazite has been extracted from beach deposits in Brazil, India, Malaysia, Thailand,

China, Taiwan, New Zealand, Sri Lanka, Indonesia, Zaire, Korea, and the United States. Present-day production is from India, Malaysia, Sri Lanka, Thailand, and Brazil. In India, monazite production from titania-zircon placers is government controlled, and a domestic plant processes monazite concentrate into REE products. In southeast Asia, monazite and xenotime are won from concentrates produced during placer tin, zircon, and titania mining. Prior to 1988, when China began to dominate yttrium production, xenotime from Malaysia was the largest source of yttrium in the world. Approximately 500 t of monazite per year were produced from 1952 to 1994 as a by-product of titania-zircon production from Pleistocene sands near Green Cove Springs in Florida.

Prior to large-scale exploitation of the Mountain Pass deposit, REE production in the United States came almost exclusively from nonmarine placers, although none comes from such sources now. The Carolina monazite belt, from which a total of about 5,000 t of monazite was produced between 1885 and 1917, has considerable placer reserves that average 0.25 kg/m³ of monazite (Overstreet 1967). In Idaho, REE minerals were produced in the 1950s from placers. Dredging operations near Cascade produced about 7,000 t of monazite from gravels containing about 1 kg/m³, and monazite reserves are estimated at 38,000 t (Overstreet 1967). Bear Valley, Idaho, where monazite and yttrium-bearing euxenite were mined by dredging, contains an estimated 10,000 t of REOs along with significant niobium and tantalum, on the basis of data from Kline et al. (1953). Some Idaho placers contain xenotime, particularly those in northern Idaho, and REEs are a possible by-product of placer gold mining in that area.

Metamorphosed Early Proterozoic conglomerate mined for uranium at Blind River, Ontario, Canada, contains REEs in monazite, uraninite, and brannerite (Roscoe 1969), and was the source of minor REE production from the 1950s to 1970s and again from 1986 to 1990. The heavy minerals in this ore are believed to be primarily of placer origin with possible enrichment during metamorphism or hydrothermal activity. Of the approximately 230 Mt of ore averaging 0.1% U₃O₈ estimated to be present in the district in 1973 (Robertson 1981), perhaps half remained unmined in the early 1990s, even though uranium mining didn't end until 1996.

At Music Valley in Southern California, xenotime- and monazite-rich zones with as much as 16% REOs (including 6% Y₂O₃) in Precambrian gneiss are thought to have originated as placer accumulations (Evans 1964). At Bald Mountain, Wyoming, a paleoplacer monazite resource was identified in Cambrian conglomerate (Borrowman and Rosenbaum 1962).

REE distribution plots of monazite and xenotime from most placer deposits have pronounced negative europium anomalies (Figure 9), indicating derivation from sources containing plagioclase. In addition, placer monazite has relatively high HREE contents compared with the strongly LREE-dominated hard-rock deposits at Bayan Obo and Mountain Pass.

HREE Deposits in Peralkaline Igneous Rocks

Although many REE deposits occur in peralkaline igneous rocks and resources can be large, most such deposits are relatively low grade, and only a single deposit in Russia has been mined. Peralkaline REE deposits are typically enriched in yttrium, HREEs, and zirconium. Future development of such deposits is dependent on the markets for these elements.

REE-bearing loparite has been produced for about 50 years from nepheline syenites in the peralkaline Paleozoic Lovozero massif on the Kola Peninsula in Russia. The massif is layered and is composed of four rock suites (Vlasov, Kuz'menko, and Yes'kova 1966). The upper 30% of the massif is eudialytic syenite.

The bottom, loparite-bearing section of the massif, over 1,000 m thick, comprises 65% of its volume and consists of alternating layers of nephelinites, nepheline syenites, and associated rocks. Late syenites occur as relatively small intrusions, and late mafic dikes are rare. The main rock-forming minerals are nepheline, microcline, and aegirine with accessory arfvedsonite, hydrosodalite, natrolite, and sodalite.

The loparite mostly occurs as 0.2- to 0.6-mm grains and rarely as larger crystals (Smirnov 1977; Vlasov, Kuz'menko, and Yes'kova 1966). Loparite contents are highest in areas of greatest differentiation and in rocks enriched in nepheline. It is found primarily in porphyritic rocks with concentrations in the urtites and their feldspar-aegirine equivalents, juvite, and malignite. The ore, in banded horizons from several centimeters to several meters thick, grades 2% to 3% loparite (Hedrick, Sinha, and Kosynkin 1997). The loparite contains 38.5% titanium oxide, 30% to 36% REOs, and 10% to 12% niobium and tantalum oxides. In the 1990s, 30,000 tpy of loparite were concentrated locally from ore from two mines and shipped to Estonia and Kazakhstan for processing (Kogarko et al. 1995). Loparite mining has ceased in recent years, but renewed production is being considered. The loparite REE distribution is weakly enriched in LREEs relative to HREEs (Figure 6).

During the 1980s when yttrium demand exceeded supply, exploration for yttrium-rich REE deposits led to the discovery of zirconium and HREE-dominated resources that are associated with peralkaline syenitic and granitic rocks. Some have associated beryllium, niobium, and tantalum. These resources are large but have low REE contents compared with commercial LREE-dominated deposits. Richardson and Birkett (1996) give an overview of Canadian peralkaline rock-associated deposits and compare them with similar deposits worldwide.

An HREE-zirconium deposit at Pajarito Mountain in New Mexico containing 2.4 Mt of rock with 0.18% Y_2O_3 and 1.2% ZrO_2 (Sherer 1990) consists of a 10-km² dome-shaped syenite intrusion (Kelley 1968). The main zirconium-REE phase was found to be eudialyte (Mariano 1989a).

Foliated syenite at Kipawa Lake, Ontario, includes a 1,300-by-100-m zone of yttrium- and zirconium-rich rock that contains eudialyte, mosandrite, and britholite (J. Allan, personal communication). The Y_2O_3 content of this deposit is comparable to that at Pajarito Mountain, but grade varies widely within the deposit, which was intensely deformed during the Grenville orogeny.

The Strange Lake zirconium-HREE-niobium-beryllium deposit in Quebec-Labrador is in a circular peralkaline granite complex about 6 km in diameter (Currie 1985). Reserves are reported at 5 Mt containing 0.5% yttrium and 3% zirconium along with beryllium, niobium, and tantalum credits (Miller 1988), and total reserves in the complex could be much larger. Most of the REEs are in gadolinite, bastnasite, and kainosite (A.N. Mariano, personal communication). Alkaline complexes in the Shallow Lake and Letitia Lake areas in Labrador, about 250 km southeast of Strange Lake, also include rocks with high yttrium content (Currie 1976; Miller 1988). Granite- and syenite-associated HREE resources with Y_2O_3 contents of about 0.2% have also been identified at Bokan Mountain in southeastern Alaska (Barker and Mardock 1988) and at Thor Lake in the Northwest Territories, Canada (Trueman et al. 1988; Taylor and Pollard 1996).

A Late Proterozoic peralkaline syenite complex at Ilimaussaq in southern Greenland contains layers with as much as 27% eudialyte (Ferguson 1970); the discovery of ore bodies containing 0.12% Y_2O_3 and 1.2% ZrO_2 has been reported (O'Driscoll 1988). The richest layer is 3.5 m thick and contains about 1 Mt of rock that

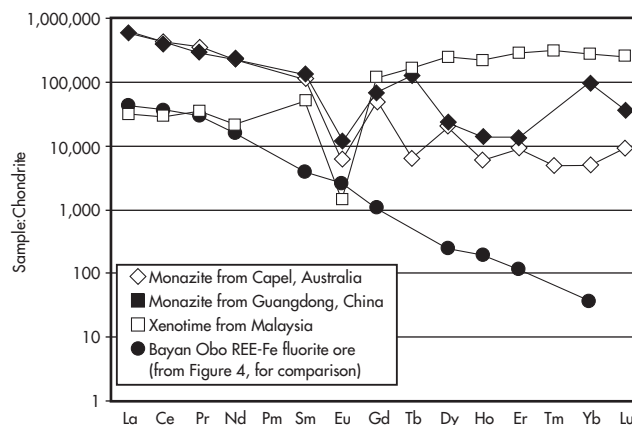


Figure 9. Chondrite-normalized plot of REE distribution (normalized to 100%) in placer monazite and xenotime (data source: Hedrick 1992)

averages 4% ZrO_2 (Steenfelt 1991). At Norra Kärr, Sweden, Middle Proterozoic eudialyte-bearing peralkaline syenite has been evaluated as a source of zirconium (Lundqvist 1980). Eudialyte from Norra Kärr contains 1.3% yttrium (Fryer and Edgar 1977).

Four Saudi Arabian deposits carrying REEs and zirconium occur in alkaline granites. The deposits include both LREE- and HREE-rich types, and estimated sizes range from 6 to 440 Mt with yttrium contents from 0.13% to 0.52% (Drysdall et al. 1984). The Brockman deposit in northern Australia has been evaluated for zirconium, yttrium, HREEs, niobium, and tantalum. The deposit, in metamorphosed lower Proterozoic rhyolite tuff, consists of 9 Mt containing 1.3% zirconium, 0.15% Y_2O_3 , and 0.12% HREEs (O'Driscoll 1988). A deposit of altered Jurassic intrusive trachyte at Dubbo, New South Wales, Australia, is probably in this class. It contains 83 Mt with 1.9% zirconium, 0.14% Y_2O_3 , 0.12% REOs, and tantalum credits (Australian Zirconia Ltd. 2000). At Pocos de Caldas, Brazil, a Mesozoic or Early Tertiary peralkaline syenite complex 30 km in diameter (Woolley 1987) contains local concentrations of eudialyte. On the Kola Peninsula, Russia, Paleozoic peralkaline syenite complexes at Khibina and Lovozero contain large amounts of eudialyte-bearing rock (Gerasimovsky et al. 1974; Kogarko et al. 1995).

Vein Deposits

REE deposits in veins are typically small in comparison to the commercial hard-rock deposits at Bayan Obo and Mountain Pass. Nevertheless, REEs were produced from two vein deposits in Africa in the past, and more recently from two such deposits in China.

In recent years, Chinese vein deposits have become important REE sources. In 1992, production from the Maoniuping mine, Sichuan Province, and the Weishan mine, Shangdong Province, together accounted for 24% of Chinese REE production (Wu, Yuan, and Bai 1996). Both are described as bastnasite-barite-carbonate veins associated with quartz syenite. They may be carbonatite dikes; published descriptions are not conclusive. The Maoniuping deposit, which is reportedly the second largest REE deposit in China (Pu, Chen, and Yang 2001), consists of swarms of veins and adjacent veinlets as much as 1,000 m long and 20 m wide that average about 2% REOs (Wu, Yuan, and Bai 1996). The ore mineral is coarse-grained bastnasite. Other REE minerals include chevkinite, xenotime, britholite, allanite, and monazite. Gangue minerals are barite, calcite, quartz, fluorite, feldspars, aegirine-augite,

and sulfide minerals. Ore at the Weishan mine occurs in veins as much as several hundred meters long and 1 m wide, with an average grade of 1.6% REOs. The mineral assemblage is similar to that at Maoniuping but also includes dolomite, amphiboles, thorite, titanium minerals, and niobium minerals (Wu, Yuan, and Bai 1996).

In South Africa, more than 50,000 t of monazite were produced in the 1950s and 1960s at Steenkampskraal (Neary and Highley 1984) from a monazite-apatite-quartz vein in Proterozoic granite. The vein, which occupies a shear zone, is about 300 m long and 1 m thick (Andreoli et al. 1994). Monazite comprises as much as 75% of the vein material (Overstreet 1967), accompanied by apatite, magnetite, and sulfide. The ore contains as much as 39% REOs with LREEs dominating HREEs and a pronounced negative europium anomaly (Andreoli et al. 1994). A similar monazite-apatite vein cuts Precambrian granite near Crescent Peak in Nevada about 30 km east of the Mountain Pass REE deposit (Castor 1991).

At Karonge, Burundi, in east Africa, quartz-barite-bastnasite-monazite stockwork veins that cut Precambrian quartzite and schist have produced small amounts of REEs (Notholt, Highley, and Deans 1990). The bastnasite and monazite have high LREEs typical of carbonatites, but secondary cerianite and rhabdophane have abnormally high or low cerium contents because of oxidation (Van Wambeke 1977). In South Africa, small REE reserves have been estimated for britholite-bearing veins in the Pilanesberg peralkaline complex (Lurie 1986).

REE- and thorium-bearing quartz veins scattered over an area of about 250 km² at Lemhi Pass on the Idaho–Montana border in the United States comprise a REE resource of 370,000 t (Staatz, Sharp, and Hetland 1979). The mineralization is mostly LREE-dominated and averages less than 1% REOs, but some veins contain as much as 0.3% Y₂O₃ and 2.0% total REOs. A small area at Diamond Creek about 50 km northwest of Lemhi Pass contains veins with similar mineralogy but with low LREE/HREE ratios. The Snowbird occurrence in northwestern Montana is an REE resource of unknown size with 0.1% to 0.2% Y₂O₃. The REE minerals are in a Cretaceous quartz-carbonate-fluorite-parisite vein considered to be of hydrothermal origin (Metz et al. 1985). Thorite-bearing quartz-carbonate-fluorite veins at Hall Mountain near Porthill in northernmost Idaho contain as much as 0.2% Y₂O₃. The Tertiary Bear Lodge trachyte-phonolite complex in Wyoming contains a minor REE resource in veins that average about 3% REOs (Staatz 1983), but the veins are narrow and commercial development is unlikely.

Veinlike deposits of apatite at Nolan's Bore, near Alice Springs in Australia, contain a significant amount of REEs. An inferred resource of 3.8 Mt of ore contains 4.0% REOs and 17% P₂O₅ (Anon. 2003). The REEs reportedly occur in the apatite and in REE minerals, with the latter possibly occurring as cross-cutting zones of cheralite.

Other Deposits

Some REE accumulations that do not fit into the deposit types previously discussed have had REE production or have been evaluated as possible sources. In recent years, a deposit near Aktyus in the Tien Shan Range of Kyrgyzstan has seen significant REE production. Although little information on this deposit exists in the literature, the deposit is said to contain complex ore from which lead, molybdenum, silver, and bismuth are also produced (Geological Survey of Kyrgyzstan 2004). The average REE content of the ore is reported to be 0.25%, with yttrium and HREEs making up 43.7% of the total REEs. The deposit consists of two stock-shaped bodies that contain synchisite-(Y), bastnasite, monazite, xenotime, and zircon (Roskill Information Services Ltd. 1996).

Some fluorspar deposits offer potential for REE production from associated REE minerals or from REEs that substitute for calcium in fluorite. Fluorspar mining at Naboomspruit in South Africa produced a small amount of monazite in the 1980s (Hedrick and Templeton 1991). About 65 t of bastnasite concentrate were produced from a fluorspar deposit in the Gallinas Mountains, New Mexico, in the 1950s (Adams 1965).

Near-economic HREE-uranium mineralization occurs as xenotime accumulations in sandstone of the Late Precambrian Athabasca Group near Wheeler River in Alberta, Canada. Similar accumulations of HREEs and uranium are in quartzite in Western Australia (Mariano 1989a).

REE deposits in Vietnam are reported to contain several million tons with grades that range from 1.4% to 5% REOs with LREE- to moderate HREE-enriched distributions. The deposits have been described as crushed zones in Paleozoic limestone affected by metasomatic processes (Premoli 1989).

Marine phosphorites have been proposed as a potential source of REEs (Altschuler, Berman, and Cuttitta 1967). Certain members of the Permian Phosphoria Formation, which are mined for phosphate in large quantities in Montana and Idaho, contain significant amounts of REEs, including as much as 0.1% yttrium (Gulbrandsen 1966).

Pegmatite REE deposits are common but generally too small or too low in grade to be commercially exploited. Production of REEs from pegmatite mined for other minerals, such as feldspar or mica, however, is possible. Allanite-bearing pegmatites are relatively common, generally with high LREE/HREE ratios. In Australia's Northern Territory, a pegmatite deposit containing 1 Mt with 4% allanite was investigated as a source of REEs (O'Driscoll 1988).

ORIGIN OF DEPOSITS

The concentration and distribution of REEs in natural deposits are dependent on several petrogenetic processes, including enrichment and complexing in late-stage magmatic or hydrothermal fluids, fractionation into mineral phases, oxidation or reduction, and redistribution during weathering. LREE enrichment in igneous rocks generally is ascribed to fractionation of HREE into minerals such as garnet and pyroxene during partial melting of source materials or during fractional crystallization. In addition, anomalously low europium/chondrite contents, a common feature in highly evolved igneous rocks of crustal derivation, are considered to be the result of Eu fractionation into plagioclase. Eu/Eu* (measured europium divided by europium calculated from interpolation between samarium and gadolinium; Henderson 1984) generally is near unity in mantle-derived rocks such as carbonatites but low in granitic rocks thought to have been derived by partial melting of crustal materials.

Lanthanum/gadolinium (La/Gd), as a measure of LREEs/HREEs, plotted against Eu/Eu* (Figure 10) is helpful in the classification of REE deposits and the interpretation of their origin. Whole rock and mineral plots for carbonatite REE deposits and laterite derived from carbonatite fall in a field of high La/Gd and Eu/Eu*. Carbonatites are considered to be mantle-derived rocks with little or no contribution from the crust. By comparison, monazite concentrates from Australian, Chinese, and Florida placer deposits plot in a tight cluster with high La/Gd and low Eu/Eu*, probably reflecting derivation from rocks that contained plagioclase or were produced by partial melting of plagioclase-bearing crustal rocks. HREE deposits in peralkaline rocks plot in a diffuse field with relatively low La/Gd and Eu/Eu*, probably because of derivation of the host peralkaline rocks from plagioclase-bearing crustal sources, and placer xenotime from Malaysia plots near the peralkaline field.

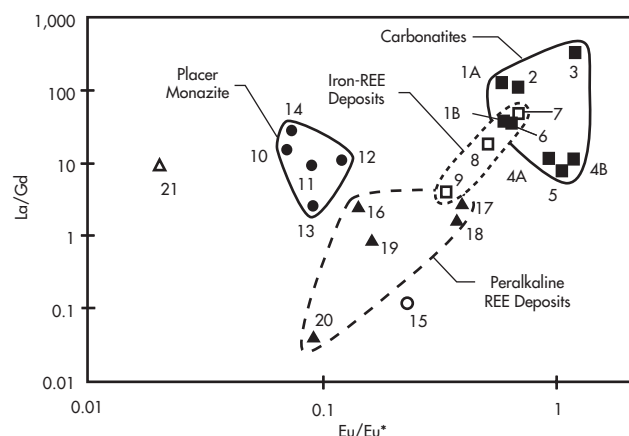
Some iron-REE deposits occupy a linear field that appears to connect the carbonatite and peralkaline HREE deposit fields, suggesting mixed crustal and mantle sources for the REEs, whereas ore from the Bayan Obo deposit plots within the carbonatite field, suggesting mantle derivation.

Most significant natural concentrations of REEs in nature are in, or associated with, alkaline igneous rocks and carbonatites. For deposits such as those at Mountain Pass, Mount Weld, Araxá, Pea Ridge, and Lovozero, this association is clear. At Bayan Obo, which emerged as the world's most important source of REEs in the 1990s, the association is less clear. Some researchers believe that the Bayan Obo deposits originated as carbonatite (Bai and Yuan 1985; Le Bas, Spiro, and Yang 1997). Others believe that the deposit is hydrothermal, but call on an alkaline igneous or carbonatite source for the fluids (e.g., Drew, Meng, and Sun 1990; Yuan et al. 1992; Campbell and Henderson 1997). Still others call on mobilization of lower crustal REEs and deposition by hydrothermal activity during a protracted period of subduction (Chao et al. 1997). In addition, the Bayan Obo iron deposits have been compared to banded-iron formation deposits (Qiu, Wang, and Zhao 1983).

Hitzman, Oreskes, and Einaudi (1992) proposed a class of dominantly Proterozoic iron oxide (copper-uranium-gold-REE [Cu-U-Au-REE]) deposits that includes the Bayan Obo, Olympic Dam, Kiruna, and Pea Ridge deposits. They suggested that these deposits formed at relatively shallow crustal levels (<4 to 6 km) from igneous-hydrothermal systems tapped by deep crustal structures associated with global rifting, possibly during break-up of a Proterozoic supercontinent. Hitzmann, Oreskes, and Einaudi (1992) did not call for mantle or carbonatite-related fluids for this class of deposits, instead proposing release of large volumes of magmatic-hydrothermal fluid during magmatic underplating of the crust. By contrast, Chao et al. (1997) proposed a protracted Paleozoic lower crustal origin for REE-rich fluids at Bayan Obo on the basis of ages of amphiboles related to REE deposition. Smith (2001) noted evidence that the Olympic Dam deposit was formed from hypersaline brines and proposed that it should be placed in a separate category from Bayan Obo, which shows no evidence of such fluids.

The Mountain Pass deposit shares features with other carbonatites in the world: (1) textural and structural features that support igneous intrusive origin (Olson et al. 1954); (2) associated alkali-rich fenitic alteration; and (3) low $^{87}\text{Sr}/^{86}\text{Sr}$ (Powell, Hurley, and Fairbairn 1966; E. DeWitt, personal communication). But the shape of the carbonatite ore body, its ultrapotassic alkaline association (most carbonatites are associated with alkaline rocks that are dominantly sodic), and chemistry (it is unusually low in iron, phosphorus, and niobium for REE-rich carbonatite) suggest that its source was different than that of most other carbonatites (Castor and Nason 2004). The chemistry of the ultrapotassic alkaline rocks at Mountain Pass suggests that they were derived from primitive or depleted mantle mixed with an enriched mantle or crustal component, and the carbonatite likely came from a similar source. The Mountain Pass LREE deposit occurs in a northeasterly-trending belt of anorogenic Middle Proterozoic plutonism that crosses the North American continent (Anderson 1983) and contains eight Middle to Late Proterozoic REE deposits (Castor 1993, 1994).

Although there are mineral and chemical similarities between the Mountain Pass and Bayan Obo deposits, there are also major differences. Like the Bayan Obo ore, the Mountain Pass carbonatite ore has extreme LREE enrichment with no europium anomalies (Figure 4) and low $^{87}\text{Sr}/^{86}\text{Sr}$. As at Bayan Obo, alkali-rich alteration is associated with the Mountain Pass carbonatite; in both areas, alteration assemblages include sodic amphibole and potash feldspar



Location No.	Deposit Name and Type	Location No.	Deposit Name and Type
1A	Mountain Pass bastnasite	12	South China placer monazite
1B	Mountain Pass monazite	13	Florida placer monazite
2	Kangankunde REE-rich carbonatite	14	Brazil placer monazite
3	Kizilçören REE-rich carbonatite	15	Malaysia placer xenotime
4A, 4B	Salitre II perovskite and anatase	16	Strange Lake peralkaline igneous HREE deposits
5	Mount Weld carbonatite	17	Kipawa Lake eudialyte
6	Maicuru REE-rich carbonatite	18	Bokan Mountain peralkaline igneous HREE deposits
7	Bayan Obo ore	19, 20	Jabal Sa'id and Jabal Tawlah peralkaline igneous HREE deposits
8	Pea Ridge breccia	21	Crescent Peak vein deposit
9	Mineville apatite		
10, 11	Western and Eastern Australia placer monazite		

Figure 10. Plot of La/Gd against Eu/Eu* for some REE-rich mineral concentrate and rock samples (data sources: Deans 1966; Fryer and Edgar 1977; Qiu, Wang, and Zhao 1983; Drysdall et al. 1984; Hedrick 1985; Roeder et al. 1987; Barker and Mardock 1988; Nelson et al. 1988; Mariano 1989a; Costa et al. 1991; G. Morteani, personal communication; L. Tucker, personal communication)

(Olson et al. 1954; Drew, Meng, and Sun 1990). The Bayan Obo and Mountain Pass deposits are both enriched in barium and fluorine (Wu, Yuan, and Bai 1996; Castor and Nason 2004). Samples of Bayan Obo ore, however, have an average BaO content of about 2.4%, and a maximum barium content of 7.7% (based on data from Chao et al. 1997), much lower than Mountain Pass ore (Table 5). The fluorine content of Bayan Obo ore, which averages more than 9%, is much higher than that of Mountain Pass ore, and Bayan Obo ore also has higher phosphorus and niobium contents (Table 5). Deposits such as those at Bayan Obo, Pea Ridge, and Mineville are clearly different from Mountain Pass in their association with large amounts of iron. Whereas Mountain Pass ore contains about 10 times as much bastnasite as monazite, Bayan Obo deposits contain approximately equal amounts of bastnasite and monazite (Y. Qiu, personal communication), although bastnasite-rich ore is selectively mined. REE-chondrite patterns for Bayan Obo show enrichment in HREEs relative to Mountain Pass (Figure 4). Finally, the ultrapotassic alkaline intrusions that are associated with the Mountain Pass carbonatite are not found at Bayan Obo. On the basis of its relatively high P, Fe, and Nb contents, if the Bayan Obo deposit has a carbonatite-related origin, it is probably to a nephelinite-carbonatite system rather than to an ultrapotassic-carbonatite system as at Mountain Pass.

The chemical compositions and mineral assemblages of most vein-type REE deposits suggest a genetic relationship with carbonatite-alkaline complexes. Such a relationship has been proposed for

the Karonge, Burundi, veins (Van Wambeke 1977). The monazite-apatite vein at Crescent Peak, Nevada, though, has REE distribution that includes a prominent negative europium anomaly that suggests a different origin than the Mountain Pass deposit 30 km away.

Although REE minerals are considered to be relatively unaffected by weathering, some lateritic REE deposits show signs of mobilization and redeposition of REEs. Residual concentration of REE minerals such as monazite is possible in laterite, and Morteani and Preinfalk (1996) reported that the REEs behaved as rather immobile elements in laterites at Araxá and Catalão in Brazil. Differences in REE distributions in different lateritic deposits may result from differences in parent rocks. For instance, Morteani and Preinfalk (1996) noted that REE distributions in the Araxá and Catalão laterites mirrored those in underlying alkaline rocks, and the very different REE distributions in the Xunwu and Longnan deposits in southern China (Figure 6) may be caused by different REE distributions in the parent rocks. As noted by Mariano (1989a), however, development of REE mineralization in laterites does not require derivation from independent REE minerals in the parent rock but may come from REEs in minerals that are less resistant to breaking down during weathering. Fractionation of the REE elements clearly takes place during weathering, as indicated by differences in REE distributions at different levels in the weathering cap above the Mount Weld carbonatite (Lottermoser 1990; Figure 8). The production of cerium anomalies (either positive or negative) during the breakdown of REE-bearing minerals in an oxygen-rich environment is to be expected; however, laterite deposits may or may not show such fractionation (compare Figure 8 with Figure 6). Mariano (1989b) proposed that differences in the mineral assemblages in carbonatite-derived laterites may result from factors other than parent rock composition, such as age, depth of weathering, and geomorphology.

TECHNOLOGY

Exploration Techniques

Geologic conditions favorable for REE deposits are widespread, but most of the world's hard-rock deposits are restricted to areas underlain by Precambrian rock. The Bayan Obo deposits, which are in Proterozoic rock, were originally discovered as ridge-forming surficial deposits of dark brown and black iron oxide (Argall 1980). Carbonatite REE deposits and many HREE deposits occur in or are associated with alkaline rocks in circular complexes, generally in Precambrian host rocks. Such complexes may be identified using aerial photography, even in deeply weathered and highly vegetated areas. Although isolated alkaline-carbonatite complexes such as Mount Weld in Australia do occur, most are in clusters or linear belts like those associated with rift zones in eastern Africa and the Araxá-Catalão belt in Brazil.

Sources for placer REE deposits include granitic rocks or high-grade metamorphic rocks, or both. Coastal monazite-bearing placers in Western Australia, Brazil, India, Sri Lanka, and the southeastern United States were derived from highly metamorphosed Precambrian shield rocks; whereas monazite and xenotime-producing placers in Eastern Australia, Malaysia, Indonesia, China, and Korea were eroded from Phanerozoic granites, including tin-rich granites. Sources of monazite, euxenite, and xenotime in Idaho placers include both highly metamorphosed Precambrian rocks and Mesozoic granitic rocks.

Because REEs are associated with thorium and uranium, radiometric exploration techniques are extremely useful in REE exploration. REE-rich carbonatite at Mountain Pass was discovered during surface prospecting for uranium using a geiger counter (Olson et al. 1954). Many other REE deposits were found by surface or airborne radiometric surveying. Although most placer REE

deposits yield only subtle radiometric signatures, careful data collection and analysis can be used to locate favorable intrabasin areas or horizons.

Geochemical prospecting using heavy-mineral concentration of active stream sediments can be very effective because most REE minerals are relatively heavy and resistant. Concentrates made by hand panning, mechanized gravity concentration, or heavy media separation can be analyzed for REEs using inexpensive multielement analytical techniques. Because many REE minerals are resistant to chemical breakdown, use of analytical methods that do not require dissolution, such as x-ray fluorescence or neutron activation analysis, is desirable, or care must be taken to use methods that assure total dissolution when using a technique such as inductively coupled plasma (ICP) spectroscopy. During prospecting for REE placer deposits in Idaho, the senior author found that favorable basins yield heavy-mineral concentrates with 1% or more cerium and 0.1% or more yttrium. Splits of heavy-mineral concentrates taken during exploration should be saved so mineral determinations can be performed using microscopic or other techniques.

Regional geochemical surveys can be used to find igneous rocks that are likely to host or be associated with REE deposits. Carbonatite deposits were delineated in Greenland using multielement analysis of fine stream sediment samples collected at a density of 1 sample/30 km² (Steenfelt 1991). The Magnet Cove alkaline-carbonatite complex in Arkansas was delineated using REEs, titanium, and fluorine contents of stream silt samples collected at a density of 1 sample/10 km² (Sadeghi and Steele 1989). Peralkaline rocks that host HREE deposits in Greenland were delineated using niobium content in fine stream sediments collected at 1 sample/6.25 km² (Steenfelt 1991). The Strange Lake deposit in Canada was discovered using regional lake water and sediment surveys, with subsequent tracing of glacially transported boulders that were initially recognized 20 km from their source (Richardson and Birkett 1996).

Biogeochemical prospecting may be useful in defining buried REE targets. REE contents of plant ash have been analyzed in areas that contain pegmatitic and vein occurrences in Finland and Canada, and extreme LREE enrichment has been noted in plant ash from the Bayan Obo area (Dunn 1995).

Normal surface exploration techniques, such as trenching and pitting by heavy equipment, are used to evaluate poorly exposed REE deposits. Exploratory dredging is used to locate beach placer deposits. In countries with low labor costs, hand pitting may be used to evaluate placer deposits or unconsolidated deposits such as those in laterite.

Drilling techniques utilized for hard-rock REE exploration and prospect evaluation are mainly core drilling and dual-tube rotary or hammer drilling. The method of choice for most heavy-mineral placer evaluations is dual-tube rotary drilling. The collection of large samples, such as are necessary to evaluate gold placers, generally is not needed because the nugget effect is not a factor in most heavy-mineral sands that contain REEs.

Because of the economic importance of differences in processing REE-bearing minerals, identification of the REE-bearing phases in prospective deposits is important. Light-colored REE minerals, such as bastnasite and monazite, may generally be distinguished by a green luminescence when illuminated by a mercury vapor light (Murata and Bastron 1956). A conventional black light with the purple filter removed may be used for this test. This luminescence, which is caused by absorption and indicates the presence of significant amounts of neodymium, has been used successfully for preliminary REE-grade determination during core logging at Mountain Pass. Because the test is based on neodymium content,

HREE minerals may not respond. Absorption bands in the visible spectrum may also be used to distinguish REE minerals with the aid of a hand spectroscope (Mertie 1960).

Geophysical methods that can be used to search for buried iron-REE deposits and some REE carbonatite deposits include gravity surveys and airborne or surface magnetic surveys. The effectiveness of such methods is based on anomalous density and magnetic susceptibility of a deposit and the associated rocks. Because many carbonatite complexes have a central carbonatite mass surrounded by mafic alkaline rocks, a common signature is a magnetic bull's-eye with high central values combined with a centrally located gravity low and a concentric gravity high. The Mountain Pass carbonatite, however, does not follow this pattern because of its high density (caused by abundant barite and bastnasite) and lack of magnetite. The Mount Weld carbonatite was discovered during interpretation of a regional aeromagnetic survey, and its detailed magnetic expression exhibits concentric zoning (Gunn and Dentith 1997). Other geophysical techniques include seismic surveys, which may be used in conjunction with drilling to determine the depth to bedrock of placer deposits.

Mining

At Mountain Pass, REE ore was mined until October 2001 in an open pit approximately 150 m deep using 80-t haul trucks and a 10-m³ shovel. Blast holes drilled at 3 to 4 m spacing were assayed for total REOs and other elements by x-ray fluorescence methods. Approximately 300,000 tpy were mined with a stripping ratio of 5:1 or higher. The ore was crushed using jaw and impact crushers at the upper lip of the pit and fed to an adjacent mill. Mining operations may be restarted in 2006 following governmental approval for pit expansion and a new tailings disposal site; however, newly enacted California mining regulations could block the resumption of mining.

At Bayan Obo, iron and REE ore is mined from two large open pits at a rate of at least 15,000 tpd using electric shovels and rail haulage (Argall 1980). Because water is lacking near the mine, crushed ore is hauled about 150 km by railroad to milling facilities at Baotou. According to Argall (1980), there was no selective mining at Bayan Obo to maximize production of any group of minerals. Originally, REO minerals may have been recovered from iron ore waste. According to Jackson and Christiansen (1993), however, REO in the iron ore is locked in slag during refining and is not recovered, and REO is produced strictly from bastnasite ore that occurs in certain zones. According to L. Drew (personal communication), during the late 1980s, REE ore came from areas mined specifically for REE production, although iron ore and REE ore were hauled on the same trains to Baotou, where most cars were routed to steel mills and some to nearby REE processing facilities. During the 1990s, REE ore enrichment by hand cobbing was witnessed at the mining operation.

Russia's loparite was mined as a primary product by underground and open-pit methods from ore bodies in the Lovozero alkali massif near the city of Revda. The mining company, Lovozersky GOK, has plans to reopen and expand its mining capacity to 2.6 Mtpy of ore; however, problems with downstream processing of loparite concentrate in Estonia probably precludes expansion in the near future.

REE placer mining is done by either dry land mining or by dredging techniques. Although Australia does not currently export monazite from titanite and zircon placer operations, descriptions of the placer mining operations in that country are probably representative of placer mining that yields monazite and xenotime elsewhere. Dredges with capacities of as much as 2,800 tph (Anon.

1987) were used in the 1980s to mine beach and dune sand deposits, particularly along the east coast. Dry land techniques, including loader and truck, scraper, drag line, or bucket wheel mining, are used for most of the heavy mineral sand mining in Western Australia (Griffiths 1984).

Processing

Flotation was used at Mountain Pass to make a bastnasite concentrate containing about 60% REOs until late in 2001. Figure 11 is a simplified flow chart for concentrate production at Mountain Pass. This concentrate was used either (1) on site as feed for chemical separation of REEs; (2) leached with dilute HCl to produce a 70% REO concentrate; or (3) shipped as is. Current sales are from stockpile. Flotation that produces concentrate containing about 60% REOs is used at Baotou to process REE ore from the Bayan Obo deposit. In Russia, loparite ore was processed using gravity and electromagnetic separation methods to produce a 95% loparite concentrate. The mill has the capacity to produce about 6,500 t of contained REOs in loparite concentrate annually, and an expansion to 12,500 t of capacity is planned.

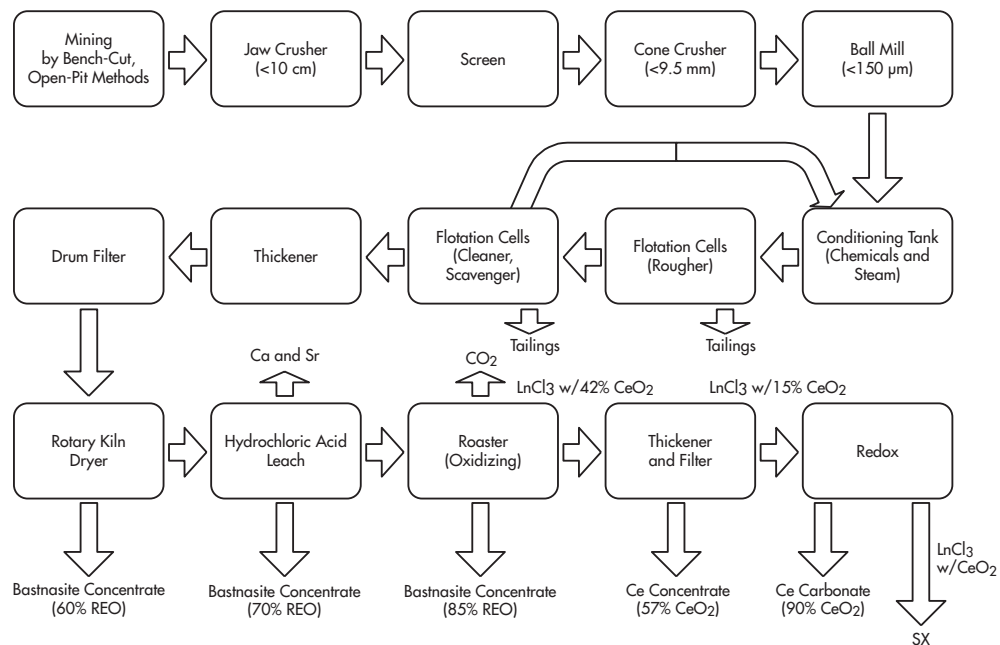
REE minerals are separated commercially from associated minerals in placer deposits using a combination of gravity, magnetic, and electrostatic techniques (Griffiths 1984). Figure 12 is a typical beneficiation flow diagram for monazite and xenotime. Gravity methods include the use of jigs, spiral and cone concentrators, and shaking tables. Sizing and preconcentration commonly is performed at the mine site by trommels, shaking screens, and gravity separation. Many dredges have such facilities on board or utilize floating preconcentration plants.

REE extraction from monazite and xenotime is accomplished by dissolution in hot concentrated base or acid solutions. During past processing of monazite ore, REEs were extracted using a concentrated solution of sodium hydroxide at 140° to 150°C (Kaczmarek 1980). After cooling, hydroxides of REEs and thorium were recovered by filtration, and thorium was separated by dissolution and selective precipitation. Monazite and xenotime also have been processed using hot sulfuric acid digestion and water leaching to remove phosphate. This is followed by selective precipitation of thorium during dilution and precipitation of REEs as double sulfates.

At Mountain Pass, bastnasite was calcined to drive off CO₂ and fluorine and leached with HCl to dissolve most of the trivalent REEs (Figure 11). The residue, which consists mostly of CeO₂, was sold as a polishing abrasive. At Baotou, Bayan Obo REE mineral concentrate is baked with sulfuric acid at 300°C to 600°C and leached with water, taking REEs into solution and precipitating other elements as waste (Chegwidden and Kingsnorth 2002). REEs are then precipitated as double sulfates and converted to hydroxides, which are leached with HCl for purification using solvent extraction (SX) and other methods. Because this method is very similar to placer monazite processing, the Bayan Obo concentrate is assumed to contain significant amounts of monazite.

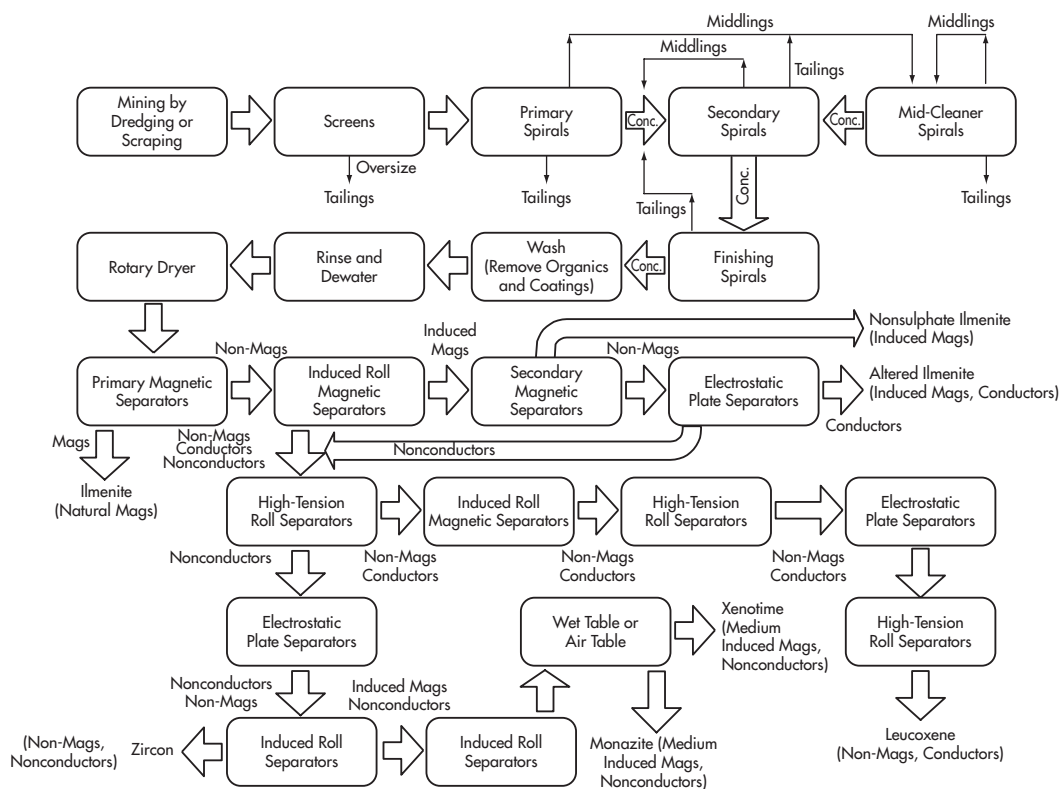
Russian loparite concentrate is produced by a mill with the capacity to generate about 6,500 tpy. The concentration process uses gravity and electromagnetic separation methods, and yields a concentrate containing 95% loparite. The mill also produces aegirine and nepheline-feldspar concentrates. If mining expansion plans move forward, expansion of the mill will produce 3,000 t of loparite concentrate in a pilot phase followed by 12,500 t in the commercial phase. Additional expansion, if warranted, would increase loparite concentrate capacity to 25,000 tpy.

Russian loparite concentrate is processed using gaseous chlorination at high temperature in the presence of reducing agents



Source: Hedrick 1992.

Figure 11. Generalized bastnasite beneficiation flow diagram (Mountain Pass, California)



Source: Hedrick 1992.

Figure 12. Generalized flow diagram for extraction of monazite and xenotime from Ti-Zr-REE mineral sand

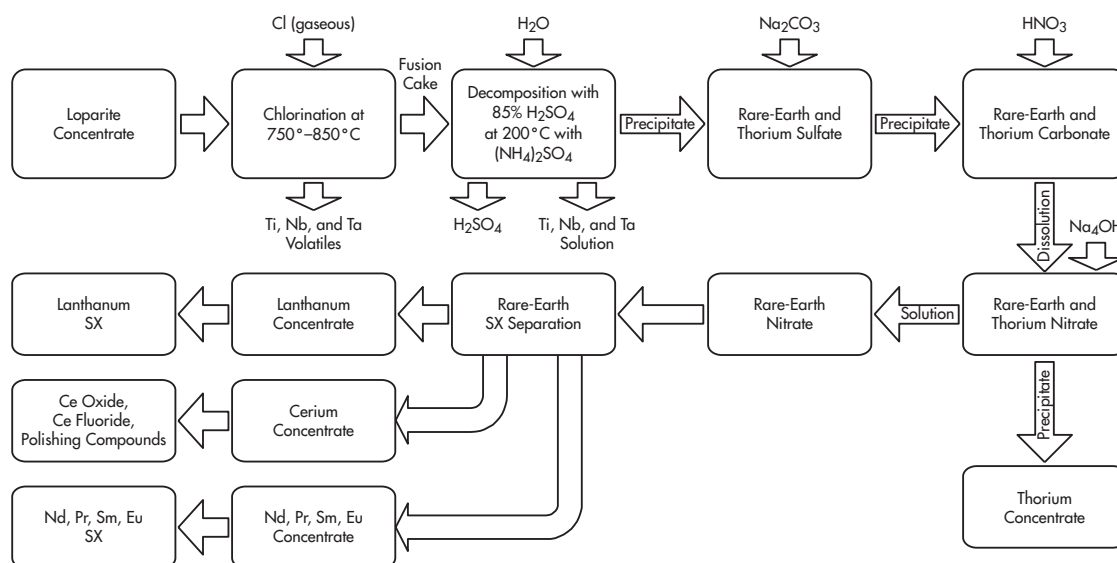


Figure 13. Loparite refinery flow diagram (Irtys, East Kazakstan Oblast, Kazakhstan, and Sillamjõe, Estonia)

(Mikhailichenko, Mikhlin, and Pattrikeev 1987). The more volatile chlorides of titanium, niobium, and tantalum are separated from the less volatile chlorides of REEs and other elements, which remain as a fusion cake (Figure 13). The fusion cake is dissolved in hot sulfuric acid in the presence of ammonium sulfate (Kosynkin et al. 1993). The solution is diluted with water, dropping out double sulfates of rare earths and thorium that are converted to carbonates by the addition of sodium carbonate. The carbonate is dissolved in nitric acid, and thorium is precipitated by raising solution alkalinity (Hedrick and Sinha 1994) or by solvent extraction. The remaining rare earth nitrate solution is separated and purified by selective precipitation and solvent extraction.

Because of their chemical similarity, the trivalent REEs are difficult to separate. Although fractional crystallization and ion-exchange techniques are used to separate them in small amounts, commercial separation generally is done using liquid-liquid solvent extraction (Kaczmarek 1980). This process consists of addition of a solvent composed of a mixture of organic compounds to the pregnant aqueous solution in a series of mixing/settling cells that allow repetitive fractionation during a more-or-less continuously flowing process. Figure 14 is a simplified diagram of the SX process used at Mountain Pass. Following precipitation and drying, specific REE compounds with purities in excess of 99.99% can be produced by this process. At Mountain Pass, a REE fraction produced during SX was treated to separate europium by reduction to the divalent state, with ultimate purification as europium oxylate (D. Witham, personal communication). Other individual REE compounds were precipitated as hydroxides, carbonates, and oxylates following complex iterative SX processes.

Specifications and Testing

Specifications for REE mineral concentrates, compounds, and metals vary depending on use. Purity specifications for some compounds may be determined by reference to Table 6. Testing of REE products mainly consists of purity determinations. In addition to specific wet chemical analytical procedures, the most effective techniques used to test products for individual REE content are x-ray fluorescence, ICP emission spectroscopy, and instrumental

neutron activation analyses. Impurities, such as phosphate, silica, lead, and thorium, may be deleterious to product utilization or the environment. The need to limit such impurities depends on use. Physical specifications, such as particle-size distribution, color, and moisture content, also are important for some products.

Advances in processing in recent years have removed markets for some relatively low-spec REE products. For instance, a 90% cerium oxide product used mainly by the glass industry and manufactured cheaply for years at Mountain Pass has been supplanted by higher-grade cerium products with little or no price increase.

ECONOMIC FACTORS

Prices

REE mineral concentrates and intermediate compounds had relatively steady price and production increases from the 1960s through the 1980s, when markets were created in response to new technologies (Castor 1994), while REE sources remained relatively steady. In recent years, prices for REE concentrates and intermediate compounds can be considered inexpensive when compared with many other mineral products (Table 6) and have lagged behind inflation. REE production increases accelerated following significant Chinese impact on the market in the 1990s (Figure 1), while prices for all REE commodities have decreased (Table 7). Therefore, despite a total annual production increase on the order of 300% since the early 1980s, the overall dollar value of the REE market has probably remained static or even decreased.

Prices for individual REOs and metals were generally lower in the late 1990s and early 2000s than in the 1960s, 1970s, and 1980s. Individual REE compounds vary widely in value (Table 7), mostly because of relative abundance and production costs. The most expensive REE is the heaviest—lutetium, which sold as the high-purity oxide for as much as \$9,000/kg in 1989 (Hedrick 1991a) and declined to a low of \$2,400/kg in 2003. Metallic REEs typically have higher prices than their equivalent oxides or other compounds. Mischmetal, a mixture of metallic REEs, was quoted at \$12.35/kg at the end of 1989 (Hedrick 1991a). During the 1980s, individual REE prices generally were static or increased slightly, but, since then, market changes have caused price decreases for individual

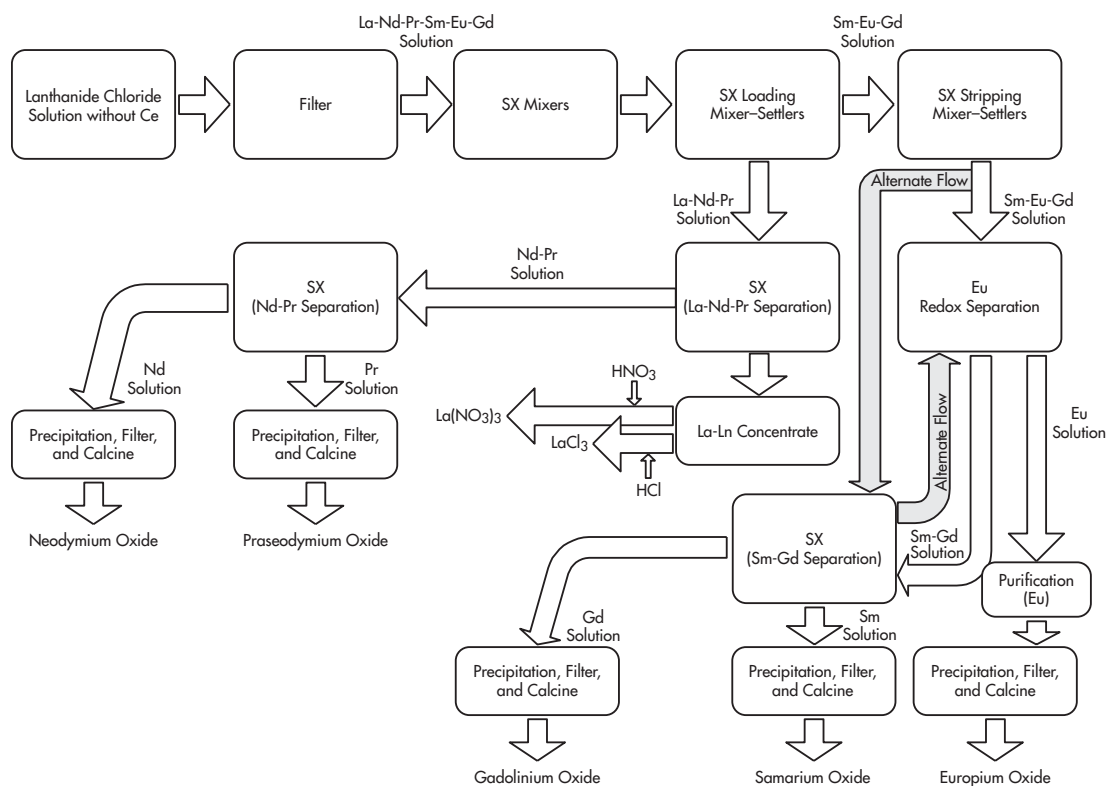


Figure 14. Rare earth SX flow diagram (Mountain Pass, California)

Table 6. U.S. prices for rare earth concentrates and compounds in 2003

Product	Purity,* %	Quantity, kg	Price,† \$/kg‡
Concentrates§			
Bastnasite concentrate, unleached	58–63	500	3.64 (contained LnO basis)
Bastnasite concentrate, leached	68–73	500	4.08 (contained LnO basis)
Bastnasite concentrate, leached and calcined	85–90	500	5.51 (contained LnO basis)
Lanthanum hydrate	75 minimum	907	5.51 (contained LnO basis)
Lanthanum-lanthanide chloride	46	159	3.20 (contained LnCl basis)
Oxides**			
Lanthanum	99.5	1	12.00
Cerium	99.5	1	18.00
Praseodymium	99.5	1	30.00
Neodymium	99.5	1	18.00
Samarium	99.9	1	58.00
Europium	99.99	1	1,120.00
Gadolinium	99.9	1	55.00
Terbium	99.9	1	440.00
Dysprosium	99.5	1	90.00
Holmium	99.9	1	245.00
Erbium	99.9	1	135.00
Thulium	99.9	1	1,950.00
Ytterbium	99.9	1	360.00
Lutetium	99.9	1	2,400.00

* Purity as total lanthanide (Ln) oxides equivalent.

† Prices are nominal and subject to change on a daily basis, priced on a contained Ln oxide or Ln chloride basis.

‡ Prices for metric-ton quantities or long-term contracts are typically lower.

§ Rare earth concentrate prices from Molycorp, Inc., free on board (f.o.b.) Mountain Pass, California.

** REO prices from Hefa Rare Earth Canada Co. Ltd., 1 kg quantity, f.o.b. Vancouver, Canada.

Table 7. Comparative U.S. prices for rare earth metals and oxides, US\$/kg

Oxides*	Year				
	1963†	1973‡	1983§	1993**	2003††
Lanthanum	12	10	19	19	12
Cerium	17	11	20	23	18
Praseodymium	88	71	130	37	30
Neodymium	66	26	80	88	18
Samarium	99	66	130	66	58
Europium	1,411	992	1,900	992	1,120
Gadolinium	176	99	140	121	55
Terbium	860	606	1,200	827	440
Dysprosium	187	88	110	132	90
Holmium	254	265	650	485	245
Erbium	187	99	200	143	135
Thulium	2,756	2,205	3,400	2,750	1,950
Ytterbium	331	187	225	220	360
Lutetium	7,661	4,409	5,200	5,500	2,400
Yttrium	119	66	94	80	52

Metals**	Year				
	1963§§	1973***	1983†††	1993†††	2003§§§
Lanthanum	309	88	125	150	25
Cerium	304	88	125	350	30
Praseodymium	386	353	310	540	70
Neodymium	386	220	260	340	30
Samarium	397	298	330	300	80
Europium	3,307	5,952	7,500	7,600	1,600
Gadolinium	463	463	485	500	78
Terbium	2,315	1,543	2,800	2,800	630
Dysprosium	661	265	300	500	120
Holmium	661	606	1,600	1,400	350
Erbium	664	309	650	725	180
Thulium	8,378	5,291	8,000	6,500	3,000
Ytterbium	1,047	507	875	1,200	484
Lutetium	9,370	12,125	14,200	13,000	4,000
Yttrium	717	309	430	340	96

* REO prices from U.S., French, and Chinese producers.

† Cerium and lutetium prices from American Potash & Chemical Corp., 2–99-lb quantity, f.o.b. Chicago, Illinois; all other REO prices from Michigan Chemical Corp., 2–99-lb quantity, 99.9% purity, f.o.b., St. Louis, Missouri.

‡ REO prices from Research Chemicals, Inc., 2–49-lb quantity, 99.9% purity, f.o.b., Phoenix, Arizona.

§ REO prices from Research Chemicals, Inc., 1–5-kg quantity, 99.9% purity, f.o.b., Phoenix, Arizona.

** Holmium, thulium, ytterbium, lutetium, and yttrium oxide prices from Rhône-Poulenc Basic Chemicals Co., 1-kg quantity, f.o.b. Phoenix, Arizona; all other oxide prices from Molycorp, Inc., 25–300-lb quantity, f.o.b. Mountain Pass, California.

†† REO prices from Hefa Rare Earth Canada Co. Ltd., 1-kg quantity, 99.5%–99.99% purity, f.o.b. Vancouver, Canada.

‡‡ Rare earth metal prices from U.S., French, and Chinese producers.

§§ Rare earth metal prices from American Potash & Chemical Corp., 1–4-lb quantity, f.o.b., Chicago, Illinois.

*** Rare earth metal prices from Research Chemicals, Inc., converted from 2–10-lb ingot price, f.o.b., Phoenix, Arizona.

††† Rare earth metal prices from Research Chemicals, Inc., 1–5-kg quantity, ingot price, f.o.b., Phoenix, Arizona.

‡‡‡ Rare earth metal prices from Rhône-Poulenc Basic Chemicals Co., 1–5-kg quantity, ingot price, f.o.b., Phoenix, Arizona.

§§§ Rare earth metal prices from Hefa Rare Earth Canada Co. Ltd., 1-kg quantity, 99.5%–99.99% purity, f.o.b. Vancouver, Canada.

Table 8. REE uses and applications by industry

Automotive	Catalysts for pollution control; catalytic converter catalyst substrate; rechargeable batteries; fuel cells; colored plastics
Ceramics	Oxygen sensors; structural ceramics for bearings; jet engine coatings; investment molds; refractories; pigments
Chemicals	Oil refinery fluid cracking catalysts; pharmaceuticals; water treatment; catalysts; moisture control, dryers, and detection
Defense	Lasers; missile guidance and control; visual displays; radar; electronic countermeasures; communication; shielding
Electronics	Capacitors; cathodes; electrodes; semiconductors; thermistors; traveling wave tubes (TWTs); radio frequency circulators and toroids; yttrium iron garnet (YIG) ferrites
Glass	Polishing compounds; decolorizing; coloring; increase refraction; decrease dispersion; radiation stabilization; absorber
Illumination	Trichromatic fluorescent lamps; mercury lamps; carbon arc lamps; gas mantles; auto headlamps; long-glow phosphors
Magnets	Speakers and headphones; linear motors; antilock braking systems; tape and disk drives; gauges; electric motors; pumps; ignition
Magnetostrictive	Sonar systems; precise actuators; precision positioning; vibratory screens; speakers; ultrasonics to kill bacteria
Medical	Contrast agents; magnetic resonance imaging (MRI); positron emission tomography (PET); radioisotope tracers and emitters
Metallurgy	Alloying agents in aluminum, magnesium, iron, nickel, and steel alloys; superalloys; pyrophoric alloys; lighter flints; armaments
Phosphors	Cathode-ray tubes (CRTs); fluorescent lighting; radar and cockpit displays; x-ray intensifying screens; temperature sensors
Other	Simulated gemstones; textiles; magnetic refrigeration; hydrogen fuel storage; lubrication; photography; nuclear uses

REE commodities. Samarium oxide, for which demand often exceeded supply during the late 1980s, sold for \$187/kg in 1988 but currently is available at \$58/kg because neodymium-iron-boron magnets have supplanted much of its market share. Europium oxide also has decreased in price from about \$2,000/kg in 1980 to \$1,120/kg in 2003. REE prices are generally lower for metric-ton quantities or long-term contracts.

Yttrium raw materials varied greatly in price during the 1980s, selling for as much as \$50/kg for contained Y₂O₃ in a 60% concentrate in the mid-1980s, retreating to \$32/kg by 1989. In the 1990s, yttrium-enriched ion-adsorption lateritic clays from southern China began supplying increasing amounts of low-cost yttrium oxide, significantly reducing demand for other yttrium concentrates derived from monazite and xenotime. The availability of low-cost yttrium oxide (\$7 to \$10/kg in metric-ton quantities in 2003) has essentially eliminated the competition in yttrium concentrate.

Rare Earth Uses and Markets

REEs are used in a wide variety of applications (Table 8). Comprising one of the widest ranges of consumer products of any element group, their usage is believed to be a significant economic indicator. Traditional REE applications in lighter flints, carbon arc lighting, and iron and steel additives have declined from 75% of the overall international REE market in the 1950s to about 20% in the 2000s.

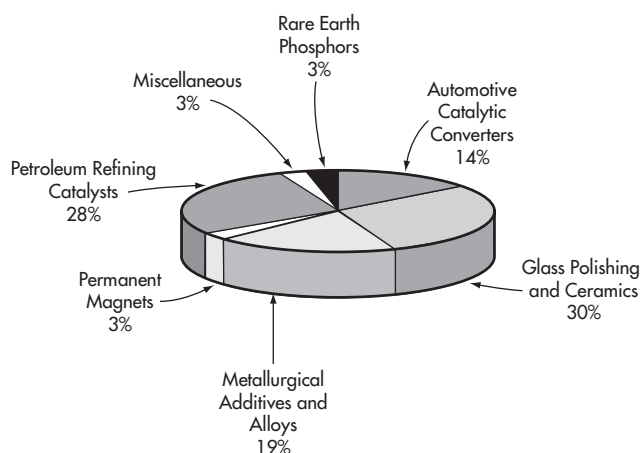


Figure 15. Rare earth markets by weight

Uses in glass polishing and ceramics are the largest market for REE commodities by weight (Figure 15). Substantial amounts of cerium concentrates and cerium oxide are used in glass-polishing applications. The automotive catalyst industry also consumes significant REEs by weight, using cerium carbonate and cerium oxide in the catalyst substrate and as a component of the converter's oxidizing catalyst system. During the 1980s, REE production increases resulted from the rising use of cerium in automotive catalytic converters (O'Driscoll 1988). The use of lanthanum-rich mixed REE compounds in fluid cracking catalysts (FCCs) in petroleum refining also has been a major market (Figure 15). Although this application initially declined substantially in the mid-1980s when legislation mandated the use of unleaded fuels, the yield of gasoline and other light-fraction products was so reduced that consumption of REE-containing FCCs were restored. Phosphors, electronics, and laser crystals provide relatively minor markets by weight, although most are high value.

Although it only comprises 3% of REE production by weight, the phosphor market is probably the most important in terms of dollar value. Beginning in the 1960s, color television manufacturers spurred demand for high-value REE phosphors based on yttrium and europium; later, gadolinium and terbium compounds were added as phosphors. More recently, their use in trichromatic phosphors in fluorescent lighting resulted in increased production.

The introduction of high-strength samarium-cobalt permanent magnets developed by Karl Strnat in the 1970s, particularly for use in small electric motors and headphones, created a dynamic new REE market. Although higher-strength, lower-cost neodymium-iron-boron permanent magnets are now substituted for the more expensive samarium-cobalt magnets in most applications, samarium-cobalt magnets are still used in applications requiring higher temperatures.

Proposed new uses have increased awareness of potential profits in REE raw materials. Superconducting substances containing lanthanum or yttrium have been in the spotlight since 1986. Volume markets for these substances, however, await further technological breakthroughs. New methods have been devised for REEs used in hydrogen-based refrigeration and energy storage. Market expansion for yttrium has provided an incentive for increased production from HREE deposits. In addition to its use in television, computer, and lighting phosphors, yttrium has found increased use in stabilized-zirconia ceramics applied in structural parts, bearings,

oxygen sensors, simulated gemstones, golf clubs and shoe cleats, shirt buttons, and coatings in the exhaust section of jet engines.

Although worldwide demand for REEs has had a general upward trend for many decades, REEs' economics are as complex as their chemistry. Because individual REEs occur together in most deposits in fixed ratios, the economic riddle is how to balance production against market demand. To accomplish this, each REE must be assigned a factor based on its natural abundance in the ore mineral in order to develop marketing equations, such as determination of price. Complexity of these equations are enhanced by variations in separation and purification costs between the REEs. In addition, markets for individual REEs may change rapidly because of technological changes and other factors. Marketing variability may also lead to stockpiling of unmarketable REE fractions and products by producers.

The principal source of REE ores is China, with smaller amounts available from India, Kazakhstan, Kyrgyzstan, Malaysia, Russia, Thailand, and the United States. Refined rare earth products, including compounds, metals, and alloys, are primarily produced in China and France.

U.S. imports were dominated by Chinese material in 2003, with 75% of domestic imports, by weight. France, with 10%, was the next largest source of U.S. imports (down from 30% in 2000), and Japan was third, with 4%. France and Japan, however, do not mine REEs and source the majority of their supplies from China. Therefore, the amount of Chinese REEs that the United States actually imported in 2003 was probably 89%. For the rare earth trade categories of domestic imports, the percentage of shipments supplied by China, by weight, were as follows:

- Cerium compounds: 84%
- Yttrium compounds: 63%
- Individual REE compounds (except cerium): 64%
- Mixtures of REOs (except cerium): 97%
- REE metals (intermixed or interalloyed): 73%
- Mixtures of REE chlorides: 94%

China was the leading source of materials for all rare earth import categories except ferrocerium and other pyrophoric alloys, a small volume trade category supplied mainly from France, at 82% of the import market.

In the mid-1980s, U.S. imports exhibited a very different distribution, at lower quantities because of high REE production from Mountain Pass. The leading supplier of domestic imports in 1985 in each category by percentage of shipments by weight, were as follows:

- Cerium compounds (except oxide): France, 89%
- Cerium oxide: France, 98%
- Individual REOs (excluding cerium): France, 84%
- REE alloys (including mischmetal): Brazil, 87%
- REE metals: former U.S.S.R., 65%
- Other REE metals: Federal Republic of Germany, 21%
- Ferrocerium and other pyrophoric alloys: France, 59%

In 1985, the majority of rare earth imports came from France, at 48%, with China supplying only about 1%.

Domestic production trended upward from the 1960s, when bastnasite production from Mountain Pass became commercially available, to the 1990s. Concentrate production at Mountain Pass ceased during 2001, when the mine and mill were put on standby status. Stocks of bastnasite concentrates and some REE intermediate and purified compounds are available from stockpiles, however.

Table 9. Harmonized Tariff Schedule for rare earth commodities imported into the United States in 2004

Heading/ Subheading Codes	Article Description	Normal Trade Relations	Non-normal Trade Relations	Special Program Codes*
2530.90.8050	Mineral substances not elsewhere specified or included; rare earth metal ores, e.g., xenotime (complex phosphate) and gadolinite, ytterbite, and cerite (complex silicates)	Free	0.3¢/kg	
2612.20.0000	Thorium ores and concentrates; rare earth metal ores, e.g., monazite (thorium and rare earth phosphate)	Free	Free	
2805.30.0000	Rare earth metals, including scandium and yttrium, whether intermixed or interalloyed, ad valorem	5.0% ad valorem	31.3% ad valorem	Free A+, CA, CL, D, E, IL, J, JO, MX, 3.7% (SG)
2846.10.0000	Cerium compounds, including oxides, carbonates, hydroxides, nitrates, sulfates, chlorides, oxalates, and so forth	5.5% ad valorem	35% ad valorem	Free A, CA, CL, E, IL, J, JO, MX, 4.1% (SG)
2846.90.2010	Mixtures of rare earth oxides, including yttrium and scandium, other than cerium oxides	Free	25% ad valorem	
2846.90.2050	Mixtures of rare earth chlorides, except cerium chloride	Free	25% ad valorem	
2846.90.4000	Yttrium-bearing materials and compounds containing by weight >19% but <85% yttrium oxide equivalent	Free	25% ad valorem	
2846.90.8000	Rare earth compounds, including individual REOs, rare earth hydroxide, rare earth nitrate, and other compounds (excludes cerium compounds, mixtures of REOs, and mixtures of rare earth chlorides)	3.7% ad valorem	25% ad valorem	Free A, CA, CL, E, IL, J, JO, K, MX, SG
2844.40.0020	Other radioactive elements, isotopes, and compounds (includes promethium, gadolinium 157, and so forth)	Free	Free	
3606.90.3000	Ferrocium and other pyrophoric alloys	5.9% ad valorem	56.7% ad valorem	Free A+, CA, CL, D, E, IL, J, JO, MX, 4.4% (SG)
7202.99.5040	Other ferrosilicon alloys, containing by weight not more than 55% silicon, other (e.g., rare earth silicide)	Free	4.4¢/kg on silicon content	

* Products eligible for special tariff treatment:

A = Generalized System of Preferences (GSP) (duty-free treatment).

A+ = Only imports from least-developed beneficiary developing countries eligible for GSP under that subheading (duty-free treatment).

CA = North American Free Trade Agreement (NAFTA) for Canada (duty-free treatment).

CL = Chile Special Rate.

D = Africa Growth and Opportunity Act (duty-free treatment).

E = Caribbean Basin Initiative (CBI).

IL = Israel Special Rate (duty-free treatment).

J = Andean Trade Preference Act (ATPA).

JO = Jordan Special Rate.

K = Agreement on Trade in Pharmaceutical Products (duty-free treatment).

MX = NAFTA for Mexico (duty-free treatment).

SG = Singapore Special Rate.

Although REE raw material production is dominated by one country, worldwide REE commodity markets are complex because of the variety of ores and commodities. Also, REE separation facilities are located in various countries that import all of their plant feed material, which means that high-purity REE products may be shipped back to the countries that originally produced the REE raw material. France and Japan, which have no internal REE raw material sources, are major producers of processed REE commodities, exporting approximately \$20 million and \$15 million worth, respectively, of REE compounds and metals to the United States in 2003. Separated REE production in France is by a single company, Rhodia Electronics & Catalysis. Originally, it utilized monazite and xenotime from Australia and the United States; however, restrictions on the disposal of thorium waste forced Rhodia to shift to intermediate REE thorium-free compounds, including rare earth chlorides and nitrates. Sixteen European countries exported REE commodities to the United States in 2003: Austria, Belgium, Estonia, France, Germany, Hungary, Ireland, Italy, Liechtenstein, the Netherlands, Norway, Russia, Spain, Sweden, Switzerland, and the United Kingdom. At least 20 companies in Japan produce REE commodities that are used by that country's steel, auto, and electronics industries. Japanese REE producers have used increasing amounts of Chinese raw and purified REE materials for their industry.

GOVERNMENTAL CONSIDERATIONS

Tariff Rates, Depletion Provisions, and Government Policies

The classification of China as a most favored nation in 1978 by the United States had a strong impact on REE markets, and the U.S.

government has shown little interest in protecting domestic producers. U.S. tariff rates are shown in Table 9.

While keeping the value of its currency low, the Chinese government has aggressively promoted its REE industry. Peking University is reported to have a research staff of 1,400 scientists working on all facets of REE production and marketing (D. Witham, personal communication). Development of Chinese REE deposits does not seem to have been impeded by normal market considerations, leading to significant overproduction of REEs in recent years. Many of China's REE mines, processing facilities, and manufacturing plants are said to be underfunded (O'Driscoll 2003). In 2003, the Chinese government announced that it would assert control over its REE industry, setting up two oversight groups: one centered on the Bayan Obo-Baotou operations in the north and one that will be developed mainly around the lateritic (ionic clay) REE deposits in southern China.

Environmental Concerns

In the United States, REE mines and processing plants are required to meet the same environmental quality guidelines as other mining and chemical facilities. The U.S. Environmental Protection Agency (EPA) is responsible for setting air-, water-, and soil-quality standards for such operations nationwide, but standards for some individual states are more stringent. Reclamation requirements for mining are under state authority and differ from state to state; however, reclamation on federally owned land is overseen by agencies such as the U.S. Forest Service and U.S. Bureau of Land Management.

REE ores and commodities, as well as by-products and waste materials from REE processing, are naturally radioactive, mostly because of contained thorium. The thorium content of monazite typically ranges from 4% to 10% ThO₂, whereas thorium comprises less than 1,000 ppm in bastnasite from Mountain Pass (Mariano 1989a) and may be even lower in Chinese REE concentrate. Handling, shipping, storage, and disposal of such materials are controlled by federal and state agencies. Less than 10 t of thorium commodities, all from imported or stockpiled material, are consumed in the United States annually (Hedrick 2004b). Therefore, thorium produced during REE processing presents an expensive disposal problem for the industry.

The Rhodia plant in Freeport, Texas, extracted REEs from largely imported monazite until 1992, when the feedstock was switched to Chinese REE concentrates. Production from this operation has declined substantially in recent years. The company's La Rochelle, France, plant is now the world's only significant REE separation plant outside of China, and it imports most of its REEs as carbonates, chlorides, and nitrates from China (Chegwidzen and Kingsnorth 2002).

Although the bastnasite produced by Molycorp, Inc., at Mountain Pass has relatively low thorium, chemical processing was suspended by the California EPA in 1998, mainly because of the radioactive element content of waste involved in a spill incident. Between 1998 and the present, Molycorp has sold REE commodities from stockpile and has purchased, tested, and resold imported REE commodities. The company plans to resume production at Mountain Pass and its environmental impact statement is currently under review.

Environmental concerns centered on the disposal of radioactive waste have precluded the development of REE extraction plants in Australia, where environmental policies are mainly under state control. A processing facility in Western Australia designed to produce REEs from 15,000 t of monazite annually, originally slated to begin production in 1989, was not constructed because of lack of approval from the Environmental Protection Authority of Western Australia. Groups concerned about radioactive contamination of the environment have become active worldwide, as shown by protests of plans to begin processing REEs in Malaysia in the late 1980s. Malaysian production of xenotime ore ceased in 1994 because of environmental regulatory compliance problems, along with the collapse of market prices for xenotime.

On the other hand, consumption of REEs in automotive and industrial emission catalysts is directly dependent on environmental regulations for air pollution control. Use and composition of REE-containing refinery FCCs are functions of both the feedstock and the fuel quality required, both of which also relate back to air pollution regulations.

FUTURE TRENDS

The future use of REEs is expected to increase, especially in automotive pollution catalysts, FCCs, and permanent magnets. Rare earth applications are expected to need greater amounts of higher-purity mixed and separated products, requiring specificity in their unique properties. Strong demand for cerium, lanthanum, and neodymium is expected to continue throughout the decade as automotive and electronic usage expands with population growth. Future growth also is forecast for REEs used in lasers, fiber optics, and medical applications that include MRI contrast agents, PET scintillation detectors, medical isotopes, and dental and surgical lasers. On the other hand, demand is expected to decline over the next decade for REE phosphors used in CRTs, as flat-panel display use increases. A slight decline also is forecast for rechargeable

nickel-hydride batteries, as lithium ion batteries gain wider use in portable electronics. Long-term growth is forecast for REEs utilized in magnetic refrigeration alloys and other technologies that exhibit energy efficiency and cost benefits.

World reserves are sufficient to meet forecast world demand well into the 21st century. Several world-class REE deposits in Australia and China (Mount Weld and Maoniuping, respectively) have yet to be fully developed and contain substantial reserves. Production may resume at idle deposits that produced in the past, such as Mountain Pass, United States, and Steenkampskraal, South Africa. Other substantial reserves are contained in heavy-mineral sands deposits worldwide. As demand continues to increase, future development of new REE deposits is likely.

U.S. companies have shifted away from using radioactive REE ores, which has negatively affected monazite-containing mineral-sands operations worldwide. The cost to dispose of radioactive waste products in the United States is expected to continue to increase, severely limiting domestic use of low-cost monazite and other thorium-bearing REE ores. Worldwide demand for monazite is expected to increase in the long term, however, because of its abundant supply and its recovery as a low-cost by-product.

World REE markets are expected to continue to be very competitive in response to China's large resources, competitive prices, low-cost wages, inexpensive utilities, and minimal environmental and permitting requirements. China is expected to remain the world's principal rare earth supplier. In addition, economic growth in several developing countries will provide new and potentially large markets in Southeast Asia and Eastern Europe.

The long-term outlook is for an increasingly competitive and diverse group of REE suppliers. As research and technology continue to advance the knowledge of REEs and their interactions with other elements, the economic base of the REE industry is expected to continue to grow. New REE applications are expected to continue to be discovered and developed.

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