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## Abstract

In this report, the light rare earth oxides are defined and their use in metallurgy, magnets, ceramics, electronics, chemicals, and other applications is discussed. Currently, almost the entire world's supply of these commodities are produced from only two deposits--Bayan Obo in China and Mountain Pass in California. The essential characteristics of the Bayan Obo deposit are discussed in light of the larger family of deposits that compose Olympic Dam-type deposits, and specific geological factors are cited to explain its enormous size.

## Introduction

As a result of recent economic developments, the world's supply of light rare earth elements comes from only two sources--Bayan Obo in China and Mountain Pass in California. Environmental concerns, however, are threatening the closure of the only U.S. producer of these elements. The mineralogy of both deposits is such that the light rare earth elements are the most important of the rare earth elements. In this report, the light rare earth elements, some of the uses to which they have been applied, their mineralogy and geology, and their resources are briefly described.

The rare earth elements are the 15 chemically similar elements that range from lanthanum through lutetium. Often, yttrium, scandium, and thorium are considered as a part of the rare earth elements. This group is sometimes referred to as the "lanthanides", because lanthanum is the first in the series. The upper one half of this series is known as the "light" rare earth elements or "cerium" subgroup, and the lower one half is known as the "heavy" rare earth elements or "yttrium" subgroup. The eight light rare earth elements (table 1) include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sa), europium (Eu), and gadolinium (Gd). Promethium does not have a stable isotope and is not found in nature.

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Generally, the rare earth elements are not rare in the Earth's crust, and this is especially true for the light rare earth elements. In average crustal abundance, cerium, the most abundant of the rare earth elements, is more plentiful than nickel [58 parts per million (ppm)] and copper (47 ppm). Neodymium and lanthanum are more plentiful than cobalt (18 ppm) and lead (16 ppm). Praseodymium, samarium, and gadolinium, are more plentiful than tin (2.5 ppm). Europium, which is the scarcest of the naturally occurring of the rare earth elements, is about one half as abundant as tin (Jackson and Christiansen, 1993).

#### Uses of the light rare earth elements

The following discussion of the light rare earth elements in the form of rare earth oxides (REO) is based on summaries by Adams and Staatz (1973) and Jackson and Christiansen (1993). The light rare earth elements form the core of a small but increasingly important industry that began in 1883 when the incandescent gas mantle was developed. This mantle contained 1 percent ceria ( $\text{CeO}_2$ ) and 99 percent thoria ( $\text{ThO}_2$ ) and was in commercial production by 1891 (Neary and Highley, 1983). At the turn of the century, lighter flints that contained a complex alloy of rare earth metals, so-called "mischmetal," as the main ingredient were being manufactured. By the late 1940's, rare earth elements were an ingredient of ductile iron. In the late 1960's and early 1970's, there was a major surge in demand for rare earth elements to be used in high-strength low-alloy steels and oil-refinery catalysts. In 1995, the approximate distribution of all rare earth production by end use was: automotive catalytic converters, 44 percent; petroleum-refining catalysts, 25 percent; permanent magnets, 11 percent; glass polishing and ceramics, 9 percent; metallurgical additives and alloys, 8 percent; phosphors, 3 percent; and miscellaneous, less than 1 percent (Hedrick, 1997).

Present and potential applications of the light rare earth elements include metallurgy, magnets, ceramics, electronics, chemical, optical, medical, nuclear, and other uses. Lanthanum is used primarily in ceramic glazes and optical glass, such as camera lenses. Cerium, the chief constituent of mischmetal, is used in production of steel and other metals, where it improves the strength and ductility of aluminum alloys and raises the high-temperature properties of magnesium alloys. It is used also as radiation shielding in cathode-ray tube face plates, petroleum refinery catalysts, and ceramic capacitors and in heat-resistant alloys in jet engines. Praseodymium is a constituent of ceramic tiles, capacitors for electronics, and permanent magnets. It is mixed with neodymium for use in glassmaker's goggles. Europium, is used in colored lamps and cathode-ray tubes, where its oxide provides the red phosphor for color television. Europium is an essential constituent of control rods in nuclear reactors because it absorbs neutrons. Samarium is used mainly in permanent magnets and in glass lasers. Gadolinium is an essential component of solid-state lasers and computer memory chips. New uses for the light and heavy rare earth elements will

undoubtedly follow as technology advances and some present uses become obsolete.

### Mineralogy and geology

The rare earth elements are mined and treated as oxides. Bastnaesite ( $\text{CeFCO}_3$ ), monazite ( $\text{Ce,Th,Y PO}_4$ ), and xenotime ( $\text{YPO}_4$ ) are the three chief REO-bearing minerals. Bastnaesite is found in vein deposits, contact metamorphic zones, and pegmatites and as a rare accessory mineral in igneous rocks, most importantly in carbonatites and related veins. It contains about 70 percent REO, mostly of the light rare earth elements, and is mined in China and California as a primary ore. Exploitable deposits of bastnaesite have been found as veins and disseminations in a complex of carbonate-silicate rocks, occurring with and related to alkaline intrusives (as in California, for example), in quartz veins cutting micaceous schists and quartzite, and in fluorite-bearing veins and breccia fillings in sandstone. Bastnaesite, which is a primary source of light rare earth elements at Bayan Obo and at Mountain Pass, is susceptible to chemical weathering, which causes the REO to dissolve and combine with available phosphates. Monazite and xenotime are found in primary deposits but are recovered principally from titanium or tin placers where they occur as accessory minerals.

The distribution of rare earth elements contained in each of the three chief REO-bearing minerals is variable. Typically, cerium accounts for almost 50 percent of the contained rare earth elements in most bastnaesite and monazite. Lanthanum and neodymium make up most of the remaining light rare earth elements. Bastnaesite commonly contains less than 1 percent heavy rare earth elements, and monazite typically contains less than 3 percent. In xenotime, the light rare earth elements account for about 15 percent of total rare earth elements compared with 85 percent for the heavy rare earth elements. Individual rare earth element percentages vary for the same mineral from different locations.

Jackson and Christiansen (1993) explained that the proportions of rare earth elements contained in bastnaesite, monazite, xenotime, or other REO-bearing minerals are crucial to the success of a mineral-producing operation. Bastnaesite, which contains essentially all light rare earth elements, cannot supply heavy rare earth elements to industry. Xenotime, which contains a majority of heavy rare earth elements, can furnish few of the light rare earth elements. Monazite has a slightly better balance of light and heavy rare earth elements, but mining it for a few specific rare earth elements requires production of undesirable REO which then must be disposed.

### Production and resources

It is difficult to refine the rare earth elements to a pure form because of their reactivity, and it is even more difficult to separate them into the individual elements or compounds owing to their chemical similarity. In 1996, world production of light and heavy REO was 79,600 tonnes (t) (Hedrick, 1997). China was the leading REO producer with 50,000 t and was followed by the

United States with 20,000 t; the former Soviet Union, 6,000 t; India 2,700 t; and other countries, including Brazil, Malaysia, Sri Lanka, and Zaire, less than 1,000 t each. According to Jackson and Christiansen (1993), this output could be doubled if the operations that do not currently recover REO would do so. Of the world's resources in 1993, about 52 percent was in China; 22 percent, Namibia; 15 percent the United States; 6 percent, Australia; and 3 percent India (Jackson and Christiansen,1993). Jackson and Christiansen (1993) noted that rare earth element resources were more than sufficient to meet the demand for the predictable future, and Hedrick (1997) suggested that undiscovered rare earth element resources were very large relative to expected demand.

#### Model for Olympic Dam-type deposits

Discovery of the enormous Olympic Dam iron-copper-uranium-gold-silver-rare earth element deposit in Australia led to considerable speculation as to its origin and its relationship to other ore deposits. Several deposits, such as Great Bear Lake in Canada, Kiruna in Sweden, Bayan Obo, and others, have characteristics in common with the Olympic Dam deposit, and a descriptive model for the origin of this type of deposit was put forth by Oreskes and Hitzman (1993).

Olympic Dam-type deposits are only loosely associated with each other in some of their outward ore-body characteristics, such as morphology; that is, stratiform to cross cutting. They have no preferred host rocks and only a weak association with contemporaneous igneous activity. These deposits exhibit close association with respect to a shallow environment of formation, strong evidence of structural control, and intense hydrothermal alteration and replacement.

Oreskes and Hitzman (1993) argued that the magnetite- and hematite-dominated systems in the Olympic Dam-type deposits were formed primarily by hydrothermal processes and argue that perhaps in only one of the deposits in this class (the Great Bear Lake district) is there evidence for a direct link between the mineralization and igneous activity. Although this class of deposits is only weakly linked to contemporaneous igneous activity, the evidence of structural control is strong. In general, structural control is evident whether along regional fault systems, in major folds, or bedding planes.

The alteration patterns associated with these deposits are usually intense--iron metasomatites and replacement bodies are common, as are sodic and potassic alterations. Intense sodic and potassic alteration often occurs in the conversion of the wallrock to sodic and potassic metasomatites. Hitzman and others (1992) propose a general wallrock alteration model that progresses from sodic alteration at depth to potassic alteration at shallower levels in these ore bodies. Oreskes and Hitzman (1993) admitted that their thinking may have been biased by their experience with the Olympic Dam deposit itself and the data on the Bayan Obo deposit that was, at the time of their study, only starting to become available. At Bayan Obo, the pattern of

sodic and potassic alteration is spatially intermingled with much potassic alteration after sodic alteration.

Oreskes and Hitzman (1993) proposed a genetic spatial model for the occurrence of the Olympic Dam-type deposits, as shown in figure 1. In this figure, a postulated progression of motivating magmatic events spans locations where the subducting plate is far inboard in the continent (either back arc or pure rift) to other locations near the edge of the continent where the subducting plate has created igneous complexes associated with a volcanic arc. The span from Olympic Dam to the Bayan Obo deposits is located in the back arc and (or) rift environment and that from the Kiruna deposit and the Great Bear Lake deposit is more-closely associated with the volcanic arc environment.

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#### The Bayan Obo deposit

Bayan Obo is regarded as a hydrothermal carbonate replacement of a Middle Proterozoic dolomite (the Y8 dolomite; Drew and Meng, 1990, 1995) and the tectonic setting is postulated to be that of an intracontinental rift (Drew and others, 1990). Proterozoic age has been confirmed by  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of Bayan Obo vein riebeckite at a minimum of 1.18 Ga (Conrad and McKee, 1992). When additional data were considered, this date has been reestimated at 1.26 Ga (J.E. Conrad, U.S. Geological Survey, written commun., March 1998). The hydrothermal system, which emplaced the ore, created an alteration halo in the dolomite and associated sedimentary rocks that cover about 50 km<sup>2</sup>. A variety of veins and (or) calcite dikes that have a carbonatite-like mineralogy, cut footwall rocks, and stockworks of veins is found at several locations in the footwall.

There are two opposing opinions on the origin of the dolomitic host rock for this deposits Drew and others (1990, 1995) and Le Bas and others (1997). According to Drew and Meng (1990, 1995) who mapped the Bayan Obo mine and surrounding area, field evidence showing that the main carbonate unit which hosts the ore bodies is of sedimentary origin is indisputable. It is possible, almost certain, that when the carbonatite-derived hydrothermal system invaded the Y8 carbonate unit that chemical reactions were so violent in the vicinity of the high-grade ore bodies that it is impossible today to determine which blocks of rock are only altered or which are completely replaced. It is possible that carbonatite dikes intruded the sedimentary carbonate, but field investigations have never revealed any significant volume of calcite in this unit. In this regard, all the carbonatite dikes and veins in the footwall are calcite with an associated carbonatitic mineralization and wallrock fenitization. They did not find any field evidence to support the hypothesis that the Y8 unit as mapped was originally anything other than sedimentary rock deposited as part of a normal marine-shelf sequence. Le Bas

and others (1997), however, favored a totally magmatic origin (intrusive carbonatite) for the coarse-grained dolomite that is found in patches within the main fine-grained dolomite unit. The fine-grained unit is, in turn, also believed to have been a possible intrusive carbonatite that was recrystallized under the influence of later mineralizing fluids.

The carbonate-replacement mechanism is very efficient at trapping ores. At Bayan Obo, this mechanism was enhanced by the 350-meter-thick Y9 shale that overlies the carbonate. The mineralizing system converted the shale to a mixture of sodic and potassic metasomatites, thereby producing an impervious, tightly sealing caprock. This combined interaction of the carbonate-replacement mechanism confined by such a seal produced the perfect situation for creating an ore body.

The chief rare earth element-bearing mineral at Bayan Obo is the hydrothermal-reaction mineral bastnaesite. Estimated resources at Bayan Obo are 1,500 million tons of iron (average grade, 35 percent), at least 48 million t of rare earth oxides (average grade, 6 percent), and about 1 million t of niobium (average grade, 0.13 percent) (Drew and others, 1990). The mine is operated by the Ministry of Metallurgy Industry as an iron mine for the production of ore that is shipped directly to a steel mill for the production of rail and wire. Rare earth ore is produced as a coproduct and either stockpiled or shipped for processing at the time of mining.

## Conclusions

The light rare earth elements are essential ingredients in many of today's high-technology applications. The ores from which their oxides are produced come from two sources in the world. If environmental restrictions lead to the closing of the Mountain Pass deposit, only the Bayan Obo deposit would remain in operation. The Bayan Obo deposit is a carbonate-replacement ore body that attained its enormous size through the unusual coincidence of a number of geologic factors that include the juxtaposition of carbonate host rock under a thick overlying shale that functioned as an impervious, tightly sealing caprock, the location of the host rock and the caprock in a continental massif that was, in turn, rifted apart, thereby allowing the emplacement of an alkaline/carbonatite complex shallow in the Earth's crust.

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Table 1. Light rare earths and their properties

[ppm, parts per million. Sources: Pincock, Allen, and Holt, 1988, p. 1.2; Wellmer and others, 1988, p. 116; Jackson and Christiansen, 1993, p. 4]

Element	Chemical symbol	Atomic number	Valence	Atomic weight	Average crustal abundance (ppm)	Oxides
Lanthanum .....	La	57	3 <sup>+</sup>	138.92	29.00	La <sub>2</sub> O <sub>3</sub>
Cerium.....	Ce	58	3 <sup>+</sup> , 4 <sup>+</sup>	140.13	70.00	CeO <sub>2</sub>
Praseodymium .	Pr	59	3 <sup>+</sup> , 4 <sup>+</sup>	140.92	9.00	Pr <sub>6</sub> O <sub>11</sub>
Neodymium.....	Nd	60	3 <sup>+</sup>	144.27	37.00	Nd <sub>2</sub> O <sub>3</sub>
Promethium.....	Pm	61	3 <sup>+</sup>	145.00	---	none
Samarium.....	Sm	62	2 <sup>+</sup> , 3 <sup>+</sup>	150.43	8.00	Sm <sub>2</sub> O <sub>3</sub>
Europium .....	Eu	63	2 <sup>+</sup> , 3 <sup>+</sup>	152.00	1.30	Eu <sub>2</sub> O <sub>3</sub>
Gadolinium.....	Gd	64	3 <sup>+</sup>	156.90	8.00	Gd <sub>2</sub> O <sub>3</sub>

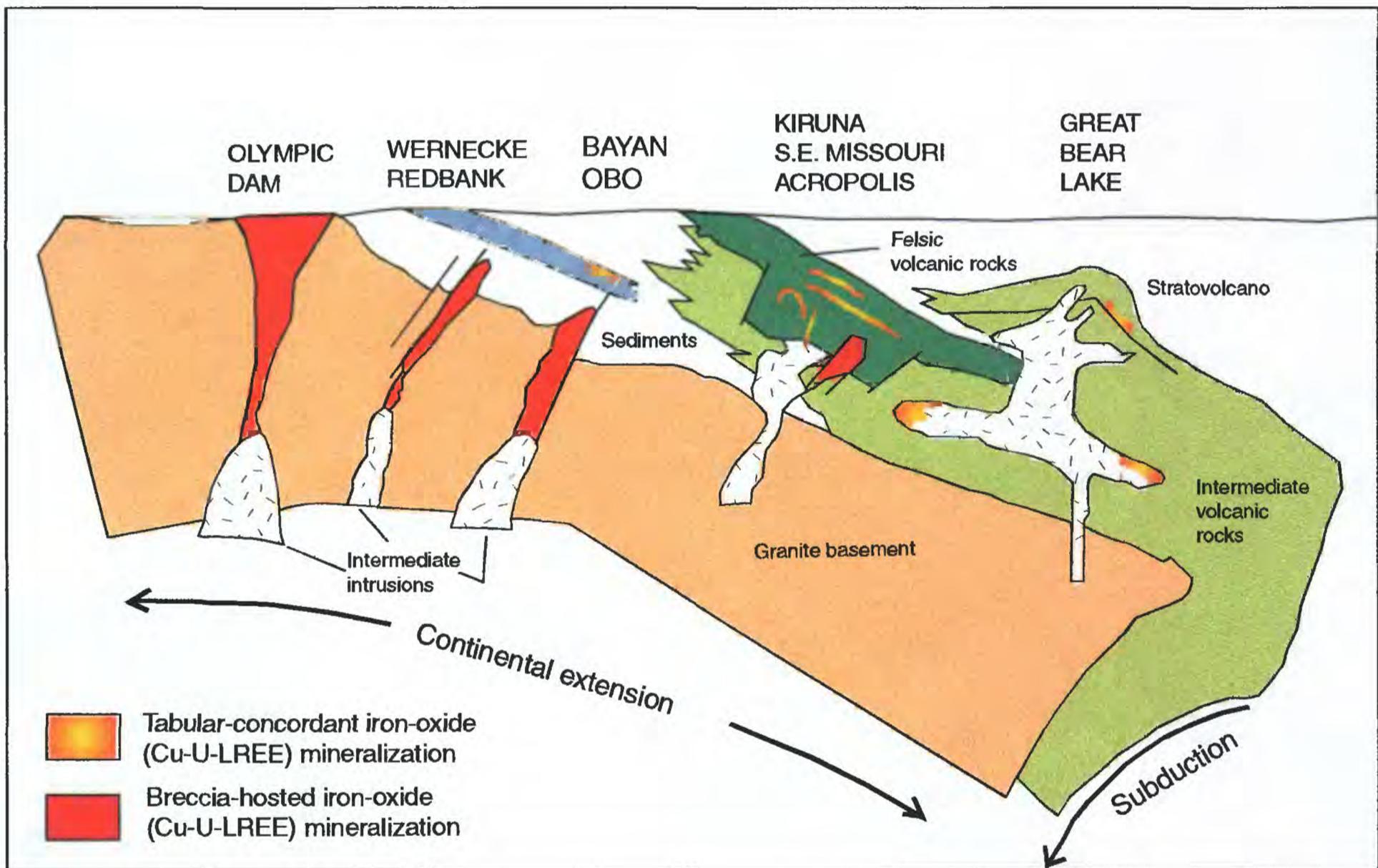


Figure 1. Mineral deposit model for the Olympic Dam-type deposits (Hitzman and others, 1992).