A "Rare" Opportunity

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Introduction

They are inside your smart phones, computers, and televisions. They are critical to military applications and the manufacture of light-weight aerospace components. Green energy enthusiasts will be interested to know they advance the capabilities of wind power generators, compact fluorescent lamps, LEDs, hydrogen storage, and hybrid and electric vehicles. They have fantastic names such as praseodymium and dysprosium, and if your ancestry hails from Sweden let your chest swell with pride as no fewer than four of them (yttrium, terbium, errbium, and ytterbium) are named after the Swedish village of Ytterby where they were first discovered. They are found primarily in alkaline rocks and carbonatites, but also at the bottom of the periodic table of elements. They are "rare earths," though the designation is a contradiction in that as a group they are more common than copper or lead, and with but one exception, individually more abundant than silver or mercury (Taylor and McLennan, 1985; Long et al., 2010).

The rare earth elements or rare earth metals consist of the 15 elements with atomic numbers ranging from 57 to 71, known as the lanthanides, and the element yttrium (atomic number = 39) which is included because of its similarities to the lanthanides. The powerful magnetism, luminescence, and strength they are capable of imparting, result in their wide-spread use in clean-energy and technology products. Rare earths can be classified chemically into light and heavy and economically into critical, uncritical, and excessive (table 1). In Earth's crust they are not particularly rare, but owing to their geochemical properties they are seldom found concentrated into economically mineable ores.

Element	Symbol	Atomic Number	%	Economic Class
Lanthanum	La	57	17.8	Uncritical
Cerium	Ce	58	38.0	Excessive
Praseodymium	Pr	59	4.2	Uncritical
Neodymium	Nd	60	15.4	Critical
Promethium	Pm	61	<0.1	Uncritical
Samarium	Sm	62	2.7	Uncritical
Europium	Eu	63	0.5	Critical
Gadolinium	Gd	64	2.3	Uncritical
Terbium	Tb	65	0.4	Critical
Dysprosium	Dy	66	2.1	Critical
Holmium	Ho	67	0.5	Excessive
Erbium	Er	68	1.4	Critical
Thulium	Tm	69	0.2	Excessive
Ytterbium	Yb	70	1.3	Excessive
Lutetium	Lu	71	0.2	Excessive
Yttrium	Y	39	13.1	Critical

Light Rare Earths *Heavy Rare Earths*

Table 1. The rare earth elements showing the percentage of total rare earths found in the upper continental crust, their economic class (Seredin and Dai, 2012), and light or heavy class.

When an economical ore is discovered, the rare-earth-bearing minerals which are separated from the ore contain multiple individual rare earths. Additional extraction and refining via numerous, complex chemical processes are required to separate the different rare earths and remove impurities. An environmental concern during mining and refining is radioactive tailings/waste from thorium and uranium, which are also often found in the ores. Rare earths are commonly produced as byproducts during the mining of other mineral commodities and as such their production volume is determined by the demand for the principal products rather than the rare earths themselves.

World Rare Earth Element Production

The Mountain Pass mine on the eastern edge of the Mohave Desert in California was the leading rare earth producer in the world from the 1960s to 1980s. At its peak the mine produced 22,000 tons/year of mostly light rare earths from a massive carbonatite which contains the rare earth-bearing mineral bastnasite (Long et al., 2010). Chinese producers entered the market in the 1980s and due in part to cheap labor and lax environmental standards, quickly began to influence the mining sector. Production at Mountain Pass decreased substantially in 1998 and was shut down in 2002 as

Background photo: These rare-earth oxides are used as tracers to determine which parts of a watershed are eroding. Clockwise from top center: praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium. Photo courtesy of Peggy Greb, US Department of Agriculture.

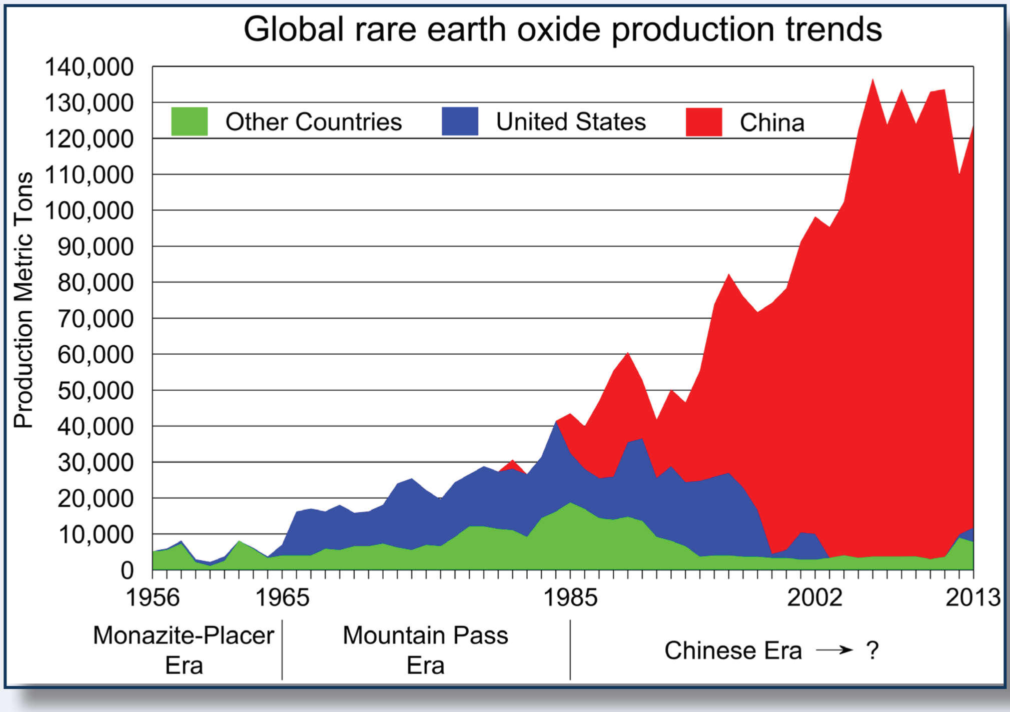

Figure 1. Global rare earth oxide production trends from 1956 to 2013. Source: USGS Mineral Commodity Summaries.

China's production began to dominate the rare earth market (fig. 1). China's production increased by more than 450% between the years 1990 to 2000 (Tse, 2011). During this time of production buildup, China's consumption of the same metals remained relatively flat and most of the product was exported. The following decade China's consumption of rare earths rose rapidly.

Currently, more than 90% of rare earth production comes from China (Gambori, 2014a). More importantly, China produces almost all of the critical heavy rare earths which are mined from weathered clay ion-adsorption deposits in its southern provinces (Gambori, 2014b). In 2009, China announced it would limit export quotas to 35,000 tons per year in order to conserve resources and protect the environment (Tse, 2011). Production and export quotas have continued with 2013 limits set at 93,800 tons and 31,000 tons respectively (Gambori, 2014a). China's policy has also encouraged exports of downstream rare earth materials, thus encouraging foreign manufacturers to relocate to China. The United States identifies import dependence upon a single country as a supply security issue, and initiated studies on rare earths in 2010. Molycorp resumed mining operations at the Mountain Pass facility in 2012 and had an estimated production of 4,000 tons in 2013 (Gambori, 2014a).

As the market demand for technology and clean-energy products grows, new sources of rare earths must be sought both domestically and through global partnerships. While traditional rare earth-containing ore bodies are not known to occur in North Dakota, alternative sources of rare earth production are being investigated on coal deposits and subsurface brines. The investigations may open a door to future rare earth production within the state.

Coal Deposits

Preliminary studies on coal deposits as a source of rare earths indicate that an "unintended production" of 40,000 tons of rare earths may be occurring annually in the United States from current coal production. Further, this "unintended production" may include over 10,000 tons of heavy rare earths (Ekmann, 2012). This raises a series of questions. Can rare earths be extracted from in-situ coal? Can selective coal mining yield material suitable for conventional rare earth extraction processes? Can coal mining waste or post-use waste (fly ash) be used as pre-concentrated sources of rare earths?

The average concentration of rare earths in coal is estimated to be about 2.5 times lower than that of the upper continental crust (fig. 2). However, because rare earths are non-volatile elements, their concentration in fly ash resulting from coal combustion is approximately three times higher than the upper continental crust. This value is close to the content of some conventional sources of rare earths. Further, abnormally enriched accumulations of rare earths have been documented in coal deposits. There are four identified means for these accumulations to develop: 1) terrigenous, rare earths input by surface water; 2) tuffaceous, falling and leaching of alkaline volcanic ash; 3) infiltrational, or meteoric ground water driven; and 4) hydrothermal, connected with ascending flows of thermal mineral water (Seredin and Dai, 2012). Such enrichment of rare earths is sometimes limited to just the roof or floor of thick coal seams. An additional important consideration is the rare earths composition, which ideally should contain higher proportions of critical metals compared to excessive metals.

Investigations have shown that coals with the highest rare earths contents have been found in lignite and subbituminous coal deposits. It is also these lower rank coals for which techniques for rare earths extraction from fly ash wastes have been developed. The Geological Survey will collect two dozen lignite samples in western North Dakota during the summer of 2015 for rare earth analysis.

In addition to looking for naturally enriched coal deposits, the U.S. Department of Energy has recently begun to study whether rare earths may be concentrated in either the coal or waste products through standard mining processes. Samples are being collected at each stage of the mining process. Preliminary findings indicate that clean coal product may have concentrated levels of rare earths. Upon combustion the rare earths are found in roughly equivalent amounts in fly ash and bottom ash

(Jerry Weisenfluh, personal communication, 2014). The U.S. Environmental Protection Agency reported in 1978 that rare earth concentrations in tailing piles were 2-3 times the amount in the feed coal. A more recent study in China (2006) reported tailing piles with more than twice the rare earth concentration of the cleaned coal (Ekmann, 2012).

Subsurface Brines

Another possible source of rare earths may be subsurface brines, which are extracted for energy recovery at geothermal power projects. Geothermal fluids heated through hot rock bodies become saturated with various minerals. The composition of the fluid is influenced by the lithology of the rocks with which it comes into contact, the temperature at which they interact, and the initial chemistry of the fluid. The high daily volumes of brine required to pass through a geothermal power plant (e.g. ~35,000 m^3 for a 50 MW station) makes it possible to recover large volumes of metal from brines with relatively low rare earth concentrations (Bloomquist, 2006). When conditions are right, the co-production of rare earths from geothermal brines can provide the economic benefit of an additional revenue stream.

There are no geothermal power stations currently in operation in North Dakota, but oil wells in the state currently generate about 1.4 million barrels of brine per day. These brines are injected into the Dakota Group as a means of disposal or injected into an oil-producing horizon as a means of enhancing oil production. Brines have traditionally only been analyzed for major ions. The North Dakota Geological Survey is in the process of collecting the deeper brines to determine their rare earth potential.

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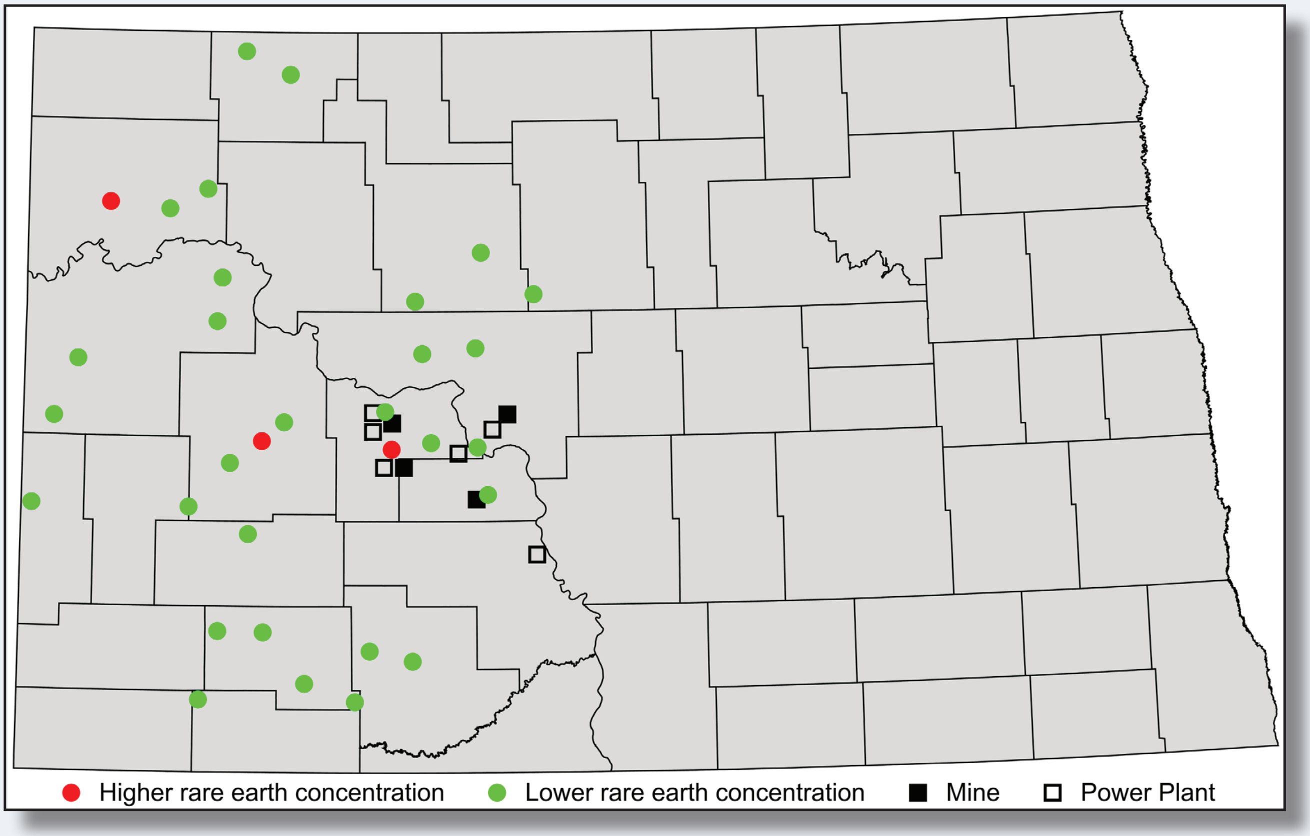

Figure 2. National Energy Technology Laboratory sample locations in North Dakota. Red dots are samples that contained more than 700 ppm of total rare earths and more than 250 ppm of heavy rare earths. Green dots are samples that contained less than 700 ppm of total rare earths and less than 250 ppm of heavy rare earths. The data was generated from the USGS COALQUAL data base. Data points were measured from ash intended to be representative of the whole core of the coal seam. Source: Eckmann (2012).