The Mountain Pass rare earth ore body in Southern California, 86 km (54 mi) south-southwest of Las Vegas, Nevada, is one of the largest, richest, and most readily mineable rare earth deposits in the world (N35° 28.74' W115° 31.98'). Its proven and probable reserves exceed 1.3 million metric tons of rare earth oxide (REO) equivalent contained in 18.4 million metric tons of ore with ~8% ore grade and a 5% cut-off grade. It contains all of the naturally occurring rare earth elements. Photo, courtesy of Molycorp, Inc.
Rediscovery of the Elements

The Rare Earths–The Beginnings

James L. Marshall, Beta Eta 1971, and Virginia R. Marshall, Beta Eta 2003, Department of Chemistry, University of North Texas, Denton, TX 76203-5070, jimm@unt.edu

Rare earths—introduction. The rare earths include the 17 chemically similar elements occupying the f-block of the Periodic Table as well as the Group III chemical family (Figure 1). These elements include the 15 lanthanides (atomic numbers 57 through 71, lanthanum through lutetium), as well as scandium (atomic number 21) and yttrium (atomic number 39). The chemical similarity of the rare earths arises from a common ionic configuration of their valence electrons, as the filling f-orbitals are buried in an inner core and generally do not engage in bonding.

The term “rare earths” is a misnomer—these elements are not rare (except for radioactive promethium). They were named as such because they were found in unusual minerals, and because they were difficult to separate from one another by ordinary chemical manipulations. In fact, except for promethium, the crustal abundance of any “rare earth” (ranging from 0.5 ppm for lutetium or thulium to 60 ppm for cerium) is greater than for silver (0.07 ppm). The most common rare earth (cerium) is more abundant than copper (55 ppm).

The importance of rare earths to modern technology cannot be overstated. Because of their unusual properties, rare earths are used in hundreds of modern applications as industrial chemical catalysts, electronic and communication devices, computers, phosphors in lighting sources, display screens, medical devices (MRI magnets), etc. In an automobile alone, rare earths can be used in catalytic converters (cerium), permanent magnets (neodymium and samarium), electric sensors (yttrium), optical

Figure 1. The “rare earths” are defined by IUPAC as the 15 lanthanides (green) and the upper two elements of the Group III family (yellow). These elements have similar chemical properties and all can exhibit the +3 oxidation state by the loss of the highest three electrons (two s electrons and either a d or an f electron, depending upon the particular element). A few rare earths can exhibit other oxidation states as well; for example, cerium can lose four electrons—4f^15d^16s^2—to attain the Ce^4 oxidation state.

Figure 2. Metallic gadolinium is ferromagnetic at room temperature, with a Curie point of 19°C. In ice-water the metal is attracted by a magnet (left) but in warm water it loses its magnetism (right). This phenomenon was discovered in 1935 by Georges Urbain (1872–1938), the co-discoverer of lutetium. Demonstration by the authors in ACS tours.
displays (yttrium, europium, terbium), hybrid batteries (lanthanum), and electronic devices (gadolinium). A classic laboratory example of the unique properties of rare earths is the unusual Curie point of metallic gadolinium (Figure 2).

The main production centers of the rare earths. Until recently, the rare earth market was dominated by the United States (Mountain Pass, California). In the previous HEXAGON “Rediscovery” article, the authors visited the Borax Visitor Center and its associated mine in Southern California. If one then proceeds 144 miles eastward, one reaches Mountain Pass in the Clark Mountain Range, the highest point (4,730 feet) on Interstate 15 before reaching the Nevada border. Mountain Pass is the site of the Molycorp Inc. open-pit rare earth mine (Figure 3) was once the world’s largest provider of rare earths, and after a brief hiatus when it successfully worked to achieve mandates of the EPA, again became one of the world’s major providers of the valuable commodity.

The major ore of the Mountain Pass mine is bastnäsite, a mineral with the formula (RE)(CO)3F, where RE = rare earth (Figure 4). Geologically speaking, bastnäsite is not a “carbonate,” which is laid down by a sedimentary process, commonly of organic origin, e.g., limestone, CaCO3. Instead, the mineral is a “carbonatite,” an igneous mineral produced in carbon dioxide-rich magmas. Rare earth carbonatites are typically formed deep in the upper mantle, from which they are later uplifted to the surface of the Earth. The process creating such surface exposures of rare earth carbonatites is quite unusual, and rare earth mines are at a premium globally.

Recently, China has assumed a major role in the industrial production of rare earths, and this past year a presentation by CBS “60 Minutes” has described the U.S.’s concern of China’s market dominance of such a strategic material. The major competitor to the Molycorp rare earth enterprise is the Bayan Obo Mining District of Inner Mongolia, China (N41° 46.97 E109° 58.42), whose bastnäsite ore is not processed on site (like Molycorp) but instead 130 kilometers south at Baotou (city center: N40° 39.38 E 109° 44.70), “China’s rare earth capital” (Figure 5). Baotou is a city of some notoriety because of its industrial pollution. The “toxic nightmarish lake” into which the Baotou steel rare earth (group) high-tech company dumps its sludge has been vividly described.

Figure 3. The entrance to Molycorp, Inc.’s, Mountain Pass mine, CA (N35° 28.35 W115° 31.70). The view is north; the rim of the open-pit mine is on the horizon. (See the cover for an aerial view of the mine).
Other sources of rare earths are rare earth phosphates (monazite and xenotime, (RE)PO₄) and “ion-adsorption ores.” Monazite and xenotime sand sources are scattered worldwide, but ion-adsorption ores are found only in southern China. These latter deposits were formed by “geological chromatography” where surface granite is leached to clay layers below. This leaching process favors Ln³⁺ ions so that insoluble cerium (Ce⁴⁺) is retained at the surface. The lower clay layers are rich in both lanthanum and yttrium and have a remarkably consistent concentration of all the other rare earths. Notable ion-adsorption mines in southeastern China include those within several kilometers of the village of Longnan (N24° 54.65 E114° 47.39), Ganzhou (prefecture), Jiangxi (province) (ca. 300 kilometers north of Hong Kong). In ion-adsorption mining, holes are drilled into the rock into which leaching solutions are injected and then withdrawn and allowed to evaporate, precipitating out the soluble rare earth salts.

“Light” and “heavy” rare earths. Because of the “lanthanide contraction,” as one proceeds to the right in the f-block of the Periodic Table, the ionic radius (⁺³) decreases from 1.17 Å for lanthanum to 1.00 Å for lutetium—and the density correspondingly increases. Hence, the lanthanides can be divided into the “light” lanthanides, including La, Ce, Pr, Nd, Sm, Eu, and Gd (left-hand side of the Periodic Table), and the “heavy” lanthanides, including Tb, Dy, Ho, Er, Tm, Yb, and Lu (right-hand side). Yttrium, with an ionic radius of 1.04 Å, resembles the heavy lanthanides, which fit more easily into the crystalline lattices of yttrium compounds.
giving rise to minerals such as gadolinite or xenotime, rich in yttrium and the heavy rare earths. The “light” rare earths are more commonly found in bastnäsite or monazite. Scandium, with a smaller radius of 0.088 Å tends to be an outlier and can occur also in specialized minerals, such as euxenite, a radio-active niobate-tantalite.

The original Bastnäs Mine. The first rare earths—yttrium and cerium—were discovered in Swedish mines (Figure 6). Yttrium was found in 1794 in gadolinite, (RE)2FeBe2Si2O10, from the Ytterby Mine of Sweden (Figure 7) by Johan Gadolin (1760–1852) in Åbo, Finland, then a Swedish territory. Cerium was discovered in 1803 in cerite, (RE,Ca)9Fe(SiO4)6(SiO3OH)3(OH)3, from the Bastnäs Mine (Figure 8) in Sweden by Jöns Jakob Berzelius (1779–1848) and Wilhelm Hisinger (1766–1852) (Figures 9, 10). The mineral cerite was originally described in 1751 by Axel Fredrik Cronstedt (1722–1765), the discoverer of nickel, as “Ferrum calciforme terra quaquad incognita intime mixtum” [Iron calx with an unknown earth] (Figure 11). Berezelius and Hisinger called it “Bastnäs tungsten” (“Bastnäs heavy stone”). They named the separated new element “cerium,” after the first asteroid Ceres discovered two years previously (Figure 12). The element was simultaneously discovered by Martin Heinrich Klaproth (1743–1817) in Berlin, who had obtained a sample of cerite from the same Bastnäs Mine; he called it “ochroite” from its yellow color (Figure 13). A decade later Hisinger and Berzelius discovered bastnäsite, described by them as a “basic fluoride of cerium,” or a “fluoride-carbonate of cerium” (“Flusspatssyradt och kolsyradt cerium”); in 1841 the mineral was given its modern name of bastnäsite. The crude ore mined at Mountain Pass and Bayan Obo is granular and mixed in a matrix of other carbonates and sulfates (Figure 4), but beautiful brandy-colored crystals are sometimes found (Figure 14).

The “pioneer” of rare earths—Mosander. The discoverers of yttrium and cerite—Gadolin, Hisinger, Berzelius, and Klaproth—did not know that their new substances actually held 15 additional elements. The scientist who recognized a variety of new elements in “Bastnäs tungsten” was Carl Gustaf Mosander (1787–1858), a student of Berzelius (Figure 15). Mosander became an instructor at the Karolinska Institute in Stockholm and in 1828 was appointed custodian of the mineral collection at the Royal Swedish Academy of Sciences. He was given a laboratory at the Academy’s new building at Wallingatan 2 (N59° 20.26 E18° 34.21). The dwarf planet (asteroid) Ceres was discovered in 1801 by Giuseppe Piazzi, Catholic priest, mathematician, and astronomer (1746–1826), at the observatory he established in Palermo, Italy, at the Palazzo dei Normanni (Norman Palace) at Piazza del Parlamento, running south from Via Vittorio Emanuele (N38° 06.69 E13° 21.17). Coincidentally, the element technetium was discovered 1.7 km to the east in 1937, at the previous Institute of Experimental Physics (Royale Istituto di Fisica Sperimentale), Via Archirafi 36 (N38° 06.61 E13° 22.39), by Emilio Segrè (1905–1989) and Carlo Perrier (1886–1948).
3.52); the Stockholm building still exists and is used as an office building.3a

Mosander was a meticulous researcher, moving slowly and methodically, never jumping to conclusions. After years of research, he began to suspect that “all was not right with cerium”9b and thought that perhaps another element was present. It was known that cerium had two oxidation states, giving rise to “cerium oxide” (today known as CeO2, or ceric oxide, or ceria; and Ce2O3, or cerous oxide; respectively). Mosander suspected the unknown element was hidden in the latter compound—and he was correct, as we know today that cerium can be present in the Ce4+ or Ce3+ oxidation state, while virtually all the other rare earths are present in the M3+ oxidation state. Mosander took a sample of his cerium oxide mixture and treated it with chlorine water, which extracted out the hidden new element, in the form of a chloride. Similarly, weak nitric acid would remove the new element, giving the nitrate. Mosander named the new element lanthanum, from the Greek “to lie hidden.” (Today, the common industrial method for removing cerium from the other lanthanides uses the same method of chemical separation. First, the rare earth mixture is allowed to air-oxidize, which transforms all cerium into the more stable, insoluble oxide CeO2 (Ce4+ oxidation state), while the remaining lanthanides remain as soluble Ln3+ and can be easily extracted out).

More rare earth discoveries by Mosander9b

The observant and cautious Mosander noticed that some of his lanthanum fractions were amethyst-colored, and he suspected yet another new element. In 1840, he heated a solution of lanthanum sulfate, thereby observing a precipitate of amethyst-colored crystals (it was known by then that cerous and lanthanum salts exhibit retrograde solubility, where salts are more soluble in cold water; this solubility behavior is quite general for Ln3+ salts, especially for the light rare earths, and is particularly exaggerated for the sulfates). Repeating this process several times allowed lanthanum salts to be recovered, now white—as well as a separated amount of amethyst-red crystals. He named this new element didymium (later found by Welsbach to be actually a mixture of two different elements.)9b Today didymium working spectacles, easily procurable from on-line vendors, are used by glassblowers to filter out the blinding yellow of sodium-containing melts.

Mosander also made a careful study of yttrium, obtained from the Ytterby Mine. Again alerted by colored solutions of its salts, in 1842 he undertook its fractional crystallization. From ammonium hydroxide solutions he obtained three fractions: the first fraction yielded a dark orange oxide of an element he named erbium; the second a rose-colored oxide of another element he named terbium; and the last a white oxide of the parent yttrium.9b He could accomplish the same task by fractional crystallization of the oxalates. [Note: in 1877 the original names of “erbium” and “terbium” were reversed9b—today erbium oxide is used to produce pink ceramics and jewelry]. His results were confirmed by Berzelius, who went on to find that Gadolin’s mineral (gadolinite, in which he found yttrium) also held cerium.

With the discovery in 1802 by Anders Gustaf Ekeberg (1767–1813; the discoverer of tantalum), that gadolinite also held beryllium,9b this meant that Gadolin’s original discovery was in fact a mixture of (at least) seven new elements: yttrium, cerium, lanthanum, didymium, terbium, erbium, and beryllium—prompting Berzelius to exclaim in 1843: “What a scoop it would have been if [Gadolin] had been able to separate them.”9b

And many more rare earths were yet to be discovered! ☞
References.


In the next issue of *The HEXAGON*, we will see how these additional rare earths were found.