



Rediscovery . . . pg 40

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.

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# HEXAGON

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**Rediscovering**

**The Rare Earths**

A new series starts on page 40.





# Rediscovery of the Elements

## The Rare Earths—The Beginnings



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**Rare earths—introduction.**<sup>1</sup> 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.<sup>2</sup> 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 communica-

PERIODIC TABLE OF THE ELEMENTS																			
1A	2A	3B	4B	5B	6B	7B	8B	1B	2B	3A	4A	5A	6A	7A	8A				
H 1																He 2			
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10		
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18		
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36		
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54		
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86		
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	113	Fl 114	115	Lv 116	117	118		
Lanthanides -		Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71				
Actinides -		Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Mv 101	No 102	Lr 103				

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.

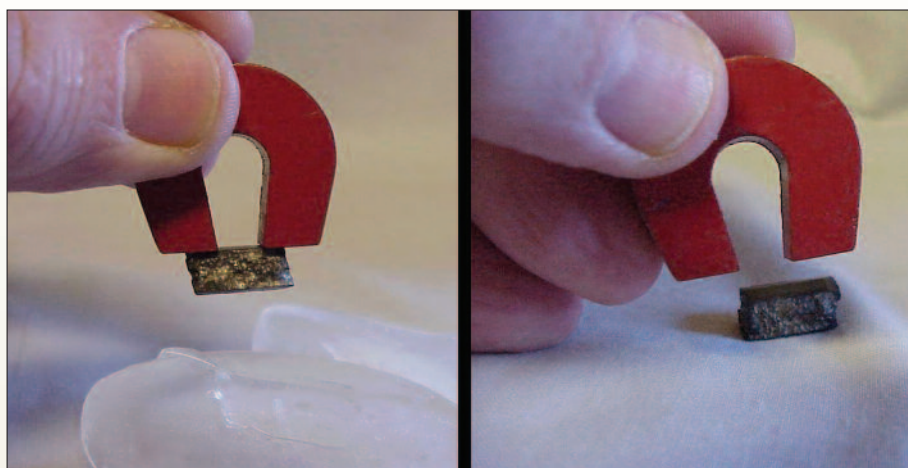


Figure 2. Metallic gadolinium is ferromagnetic at room temperature, with a Curie point of 19°C. In ice-water the metal is attracted by a magnet (left) but in warm water it loses its magnetism (right). This phenomenon was discovered<sup>11</sup> in 1935 by Georges Urbain (1872–1938), the co-discoverer of lutetium.<sup>3\*</sup> Demonstration by the authors in ACS tours.

tion 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 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).



Figure 5. The entrance to the largest producer of rare earths, the Inner Mongolia Baotou plant, 8 km west of Baotou city center. The huge industrial complex is 560 km west of Beijing and can be identified on Google maps centered at N40° 39.38 E109° 44.70. Originally a steel production plant, Baotou Company entered the rare earth business in 1958. This rolling steppe was once a vast, beautiful grassland, but now is a toxic wasteland with atmospheric coal dust and sulfuric acid, and an infamous sludge lake clearly visible on Google maps (N40° 38.22 E109° 41.33). By the 1980s, leakage from the toxic lake (including thorium discharge into the Yellow River) was damaging five surrounding villages, resulting in their complete removal. Image reproduced with the kind permission of CBS News/"60 Minutes."<sup>4</sup>

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,<sup>3k</sup> 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 (see

cover). This 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)<sub>3</sub>F, 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, CaCO<sub>3</sub>. Instead, the mineral is a "carbonatite," an igneous mineral produced in carbon dioxide-rich magmas.<sup>2</sup> 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



Figure 4. These are bastnäsite boulders lining the entrance road to MolyCorp—the stones appear as reddish (RE)CO<sub>3</sub>F crystals in a white matrix of calcite, dolomite, and barite. A check with a Geiger counter proved they were slightly radioactive, typical for a rare earth mineral. The composition for Mountain Pass bastnäsite is variable, but a rich sample procured by the authors showed a content (RE%) of La 32%, Ce 49%, Pr 4%, Nd 14%, Sm 0.5%, Gd 0.3%, Eu 0.1%, with ppm quantities of the remaining lanthanides (except promethium) and Sc and Y.

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.<sup>4</sup> 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 E 109° 50), "China's rare earth capital"<sup>4</sup> (Figure 5). Baotou is a city of some notoriety because of its industrial pollution.<sup>5</sup> In particular, the "toxic nightmarish lake" into which the Baotou Steel Rare Earth (group) High-tech Company dumps its sludge has been vividly described.<sup>5</sup>





Figure 6. The two discovery sites of the first two rare earths (yttrium and cerium) were respectively the Ytterby Mine<sup>2c</sup> near Stockholm, and the Bastnäs Mine near Riddarhyttan in the Ekomuseum Bergslagen, a region in the center of Sweden containing several national heritage sites.

Figure 7. The Ytterby mine (N59° 25.60 E18° 21.18) has been closed off, but the surrounding rock facing (right) is typical of the pegmatite geology of the area. Pegmatites have the same composition as granite—quartz, feldspar, and mica—but the crystals are larger (left). In pegmatite outcroppings in Sweden, frequently other minerals are found, such as the gadolinite (left) in which yttrium was originally found. Historically, the quartz and feldspar were mined for the porcelain industry. Directions to reach this mine have been previously published in the 2008 Spring HEXAGON.<sup>3\*</sup>



Figure 9. The entrance of the Bastnäs Mine. “Bast-näs” in Swedish means “Raffia-peninsula,” referring to the wetlands where raffia was collected in historic times and used to make baskets and even hardy skirts for hard labor. Today the wetlands about Bastnäs abound in wildflowers and strawberries and are visited by an occasional moose. The Bastnäs mine was originally an iron mine owned by Hisinger but later provided quantities of industrial cerium.



Figure 8. This map describes how to reach the Bastnäs Mine. The Swedish government wishes to leave the countryside pristine and convenient highway signs are not posted to guide the traveler. The Mine itself (A) is located at N59° 50.75 E15° 35.34. One enters the mine road off Highway 68 (which leads north from Riddarhyttan) at either B (N59° 49.99 E15° 32.99) or C (N59° 52.06 E15° 36.86). The historic Hisinger house (D) is located on Herrgårdsvägen (N59° 49.71 E15° 40.79).

Other sources of rare earths are rare earth phosphates (monazite and xenotime, (RE)PO<sub>4</sub>) and “ion-adsorption ores.”<sup>6</sup> 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 Ln<sup>+3</sup> ions so that insoluble cerium (Ce<sup>+4</sup>) 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,”<sup>7</sup> 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” lan-

thanides, 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,





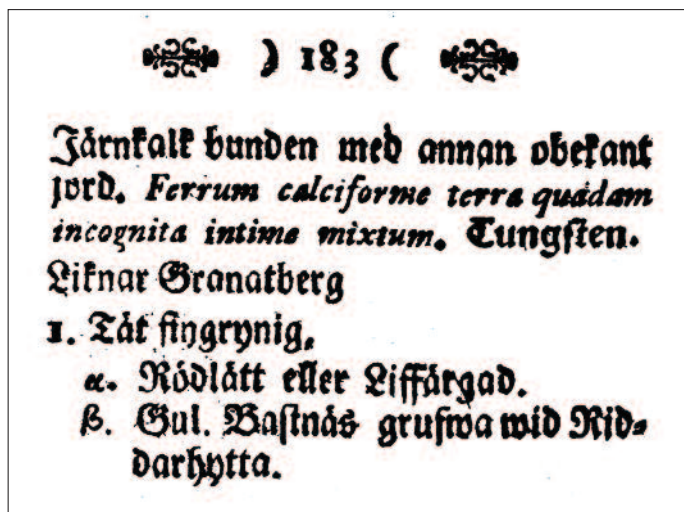


Figure 10. (Above left) Inside the Bastnäs mine, checking for radioactivity—common in rare earth mines, usually produced by thorium. Figure 11. (Above right) This is the original description by Cronstedt of cerite.<sup>8</sup> On the basis of his expert blowpipe analysis, he recognized the mineral as an iron ore with a “new earth.” He called it “Tungsten,” Swedish for “heavy stone.” He characterized it as [translated] “similar to garnet-stone./ Solid [and] fine-grained./ Ruddy or flesh-colored./ Yellow, [from the] Bastnäs Mine at Riddarhyttan.”



Figure 12. 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).<sup>31</sup>

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 radioactive 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,  $(RE)_2FeBe_2Si_2O_{10}$ , from the Ytterby Mine of Sweden (Figure 7) by Johan Gadolin (1760–1852) in Åbo, Finland, then a Swedish territory.<sup>3c</sup> Cerium was discovered in 1803 in cerite,  $(RE,Ca)_9Fe(SiO_4)_6(SiO_3OH)(OH)_3$ , from the Bastnäs Mine (Figure 8) in Sweden by Jöns Jakob Berzelius (1779–1848) and Wilhelm Hisinger (1766–1852)<sup>3b,d</sup> (Figures 9,10). The mineral cerite was originally described in 1751 by Axel Fredrik Cronstedt

(1722–1765, the discoverer of nickel<sup>3i</sup> as “Ferrum calciforme terra quadam incognita intime mixtum” [Iron calx with an unknown earth]<sup>8</sup> (Figure 11). Berzelius and Hisinger called it “Bastnäs tungsten” (“Bastnäs heavy stone”).<sup>3a</sup> They named the separated new element “cerium,”<sup>3d</sup> after the first asteroid Ceres discovered two years previously (Figure 12). The element was simultaneously discovered by Martin Heinrich Klaproth (1743–1817)<sup>3f</sup> in Berlin, who had obtained a sample of cerite from the same Bastnäs Mine; he called it “ochroite” from its yellow color<sup>3b</sup> (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”);<sup>10a,b</sup> in 1841 the mineral was given its modern name of bastnäsite.<sup>10c</sup> 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.<sup>9b</sup>

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°



Figure 15. Carl Gustaf Mosander's research proved that yttrium and cerium, the two most abundant rare earths, actually held additional elements. Like Berzelius, Mosander studied medicine but became interested in chemistry where he made a major impact studying unusual minerals of Sweden.

03.52); the Stockholm building still exists and is used as an office building.<sup>34</sup>

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"<sup>9b</sup> 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  $\text{CeO}_2$ , or ceric oxide, or ceria; and  $\text{Ce}_2\text{O}_3$ , 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  $\text{Ce}^{+4}$  or  $\text{Ce}^{+3}$  oxidation state, while virtually all the other rare earths are present in the  $\text{M}^{+3}$  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  $\text{CeO}_2$  ( $\text{Ce}^{+4}$  oxidation state), while the remaining lanthanides remain as soluble  $\text{Ln}^{+3}$  and can be easily extracted out).

#### More rare earth discoveries by Mosander!<sup>9b</sup>

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 lanthanide 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 sol-



Figure 13. Martin Heinrich Klaproth (1743–1817)<sup>3f</sup> was codiscoverer of cerium. This exhibit at the Berlin Museum für Naturkunst (Museum of Natural History; Invalidenstrasse 43; N52° 31.79 E13° 22.78) displays authentic samples of the minerals from which he discovered/co-discovered eight elements, including cerium, beryllium, titanium, chromium, strontium, zirconium, tellurium, and uranium. Always a modest and unambitious gentleman, he often gave credit to others when in fact it was his splendid research that confirmed a discovery.

uble in *cold* water; this solubility behavior is quite general for  $\text{Ln}^{+3}$  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 (1840). He named this new element *didymium* (later found by Welsbach to be actually a mixture of two different elements.)<sup>3g</sup> 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.<sup>9b</sup> He could accomplish the same task by fractional crystallization of the oxalates. [Note: in 1877 the original names of "erbium" and "terbium" were reversed<sup>9b</sup>—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.



Figure 14. This gemmy crystal of *bastnäsite*, measuring 10 mm across, is hexagonal, resembling a ruby; while simultaneously it appears as translucent coffee-colored, very much like a garnet. This crystal analyzed by EDX to give 26% La, 29% Ce, 6% Nd, and lesser amounts of Pr, Sm, Eu, and Gd. From the private collection of the authors.

With the discovery in 1802 by Anders Gustaf Ekeberg (1767–1813; the discoverer of tantalum<sup>3h</sup>), that gadolinite also held beryllium,<sup>3c</sup> 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."<sup>9b</sup>

And many more rare earths were yet to be discovered! ☺



## References.

1. F. H. Spedding and A. H. Daane ed., *The Rare Earths*, **1961**, Wiley.
2. G. K. Muecke and P. Möller, "The Not-So-Rare Earths," *Sci. Amer.*, **1988**, *258*(1), 72–77.
3. J. L. and V. R. Marshall, *The HEXAGON of Alpha Chi Sigma*, (a) **2002**, *93*(1), 9–11; (b) **2003**, *94*(1), 3–8; (c) **2004**, *95*(3), 46–50; (d) **2007**, *98*(4), 70–76; (e) **2008**, *99*(1), 8–11; (f) **2008**, *99*(2), 20–24; (g) **2011**, *102*(3), 36–41; (h) **2013**, *104*(2), 20–25; (i) **2013**, *104*(4), 84–89; (j) **2014**, *105*(2), 24–29; (k) **2015**, *106*(2), 24–29.
4. Lesley Stahl, **60 Minutes**, "Rare earth elements: not so rare after all," March 22, 2015, CBS News.
5. T. Maughan, <http://www.bbc.com/future/story/20150402-the-worst-place-on-earth> "The dystopian lake filled by the world's tech lust."
6. B. T. Kilbourn, *A Lanthanide Lanthology, Parts I and II*, **1993**, Molycorp Inc., White Plains, NY.
7. V. M. Goldschmidt, T. Barth, and G. Lunde, Skifter utg. Av det Norske Videnskaps-Akademi i Oslo I. Mat.-naturv. Klasse, **1925** No. 7, p 59.
8. A. F. Cronstedt [anonymous], (a) *Försök till Mineralogiens eller mineral-Rikets uppställing [An attempt at mineralogy or arrangement of the Mineral Kingdom]*, **1758**, Stockholm, Tryckt uti Wildiska tryckeriet, 183 (b) English translation: A. F. Cronstedt, *An Essay towards a System of Mineralogy*, **1770**, London, Edward and Charles Dilly, 201–202.
9. C. H. Evans, ed., *Episodes from the History of the Rare Earth Elements*, Kluwer Academic Publishers, **1996**. (a) J. Trofast, "The discovery of cerium," 13–33; (b) Levi Tansjö, "Carl Gustaf Mosander," 37–53; (c) F. Szabadvary and C. Evans, "The 50 years following Mosander," 55–65.
10. (a) J. J. Berzelius, *Ahandlingar I Fysik, Kemi och Mineralogi*, **1818**, 5, 64; (b) J. J. Berzelius, *Årsberättelser om Vetenskapernas Framsteg*, **1824**, 31 Mars, 201–202; (c) T. Egleston, *A Catalogue of Minerals and Synonyms*, **1892**, John Wiley, 379.
11. G. Urbain, P. Weiss, and F. Trombé, *Compt. Rend. Chim.*, **1935**, *200*, 2132–2134.

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

