Rediscovering
The Rare Earths
A new series starts on page 40.
No Time to Rest!

"There is no time to rest on your laurels." This is the mantra of the National Office and the Supreme Council. The world is changing and so are we. We barely got settled into the new National Office when we tackled the project of updating the website. People surf the web on a variety of devices of different shapes, sizes and operating systems, and so our website needs to be informative and friendly to everyone. Our website was getting that dated look, and so our National Office staff, GMC Kip Nalley, and I tackled an overhaul of our website with the assistance of the experts at Blackbaud.

The new website has a fresh, clean look no matter what platform you are viewing it on. Thanks to a cadre of brothers who reviewed and interacted with test pages, we were able to use scientific methods. We have built a more intuitive navigation system that will help you quickly find how to start a new collegiate or professional chapter, learn about outreach programs, ascertain the deadline for a report, or make a donation. You will find an interactive map to help you visualize the geographic locations of all of our chapters and acquire valuable information about each of those chapters. One of the primary goals was to use more imagery to show, instead of tell our messages. Another goal was to increase the traffic to and from the site from social media sites like LinkedIn and Facebook.

The whole process started in January of 2015 with an introspective look at who we are and who was our audience for the website. The discussion of who we are led to discussions that led us to change the tagline for the Fraternity from "Professional in Chemistry" to the broader "Professional in the Chemical Sciences" which was felt to be more reflective of our membership and the expansion of the field. Consideration of who would visit our website identified five major groups: Collegiate members, Professional members, prospective members, the faculty and administration of schools to where we are expanding, and the general public. This focused our attention on how to ensure the website is pertinent to each of these groups. Finally, we will soon launch the site. Stay tuned!

Of course, after all this work if we are simply content to say, "Look! Here it is complete!" we would be making that "resting on the laurels" mistake. Keep coming back to the site to see what is new. We have committed staff time each week to develop more material. You can help us with that. Give us your feedback. Let us know what you or your chapters are doing. Tell us your stories. It is an exciting time in the Fraternity and the world and we plan on keeping up with the times.

What other changes can you expect to see in the future? Period newsletters are a dated form of communication. This fall, we plan on delivering the information that we had included in the Chrome and Blue in a more continuous fashion on Facebook and on the website. Enabling professional brothers to break up their annual contributions into small automatic monthly deductions from their credit cards is another step we are considering.

We can’t do it alone. Please send your ideas, stories, and feedback to: National@alphachisigma.org.
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
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 (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)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 E 109° 50), “China’s rare earth capital” (Figure 5). Baotou is a city of some notoriety because of its industrial pollution. In particular, the “toxic nightmarish lake” into which the Baotou Steel Rare Earth (group) High-tech Company dumps its sludge has been vividly described.
Other sources of rare earths are rare earth phosphates (monazite and xenotime, \((\text{RE})\text{PO}_4\)) 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 \(\text{Ln}^{3+}\) ions so that insoluble cerium (\(\text{Ce}^{4+}\)) 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,
Järnfallet hunden med annan obeviss jord. Ferrum calciforme terra quadam incognita intime mixtum. Tungsten.

Litter Granathögl

1. Tät finkynig
   a. Rödlätt eller Liffärkogad.

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. 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 similar to garnet-stone. Solid and fine-grained. Ruddy or flesh-colored. Yellow, from the Bastnas Mine at Riddarhytten.”

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 Institute di Fisica Sperimentale), Via Archirafi 36 (N38° 06.61 E13° 22.39), by Emilio Segrè (1905–1989) and Carlo Perrier (1886–1948). 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, \( \text{(RE)}_2\text{FeBe}_2\text{Si}_2\text{O}_{10} \), 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, \( \text{RE}_2\text{Si}_2(\text{SiO}_4)_6(\text{OH})_3 \), from the Bastnäs Mine (Figure 8) in Sweden by Jöns Jakob Berzelius (1779–1848) and Wilhelm Hisinger (1766–1852). The mineral cerite was originally described in 1751 by Axel Fredrik Cronstedt (1722–1765), the discoverer of nickel as “Ferrum calx with an unknown earth” [Iron calx with an unknown earth] (Figure 11). Berzelius and Hisinger called it “Bastnas tungsten” (“Bastnas 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 “Bastnas 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°
it by then that cerous and lanthanum salts exhibit of amethyst-colored crystals (it was known lanthanide sulfate, thereby observing a precipitate). The observant and cautious Mosander noticed that some of his lanthanum fractions were easily extracted out. 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 Mosander*

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 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 (1840). He named this new element didymium (later found by Welsbach to be actually a mixture of two different elements).* 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.** He could accomplish the same task by fractional crystallization of the oxalates. [Note: in 1877 the original names of “erbium” and “terbium” were reversed***—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 13. Martin Heinrich Klaproth (1743–1817) was codiscoverer of cerium. This exhibit at the Berlin Museum fur 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.

Figure 14. This gemmy crystal of bastnasite, 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 tanta-lum*), that gadolinite also held beryllium,* 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.”** And many more rare earths were yet to be discovered!
References.


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4. Lesley Stahl, 60 Minutes, "Rare earth elements: not so rare after all," March 22, 2015, CBS News.


10. (a) J. J. Berzelius, Afhandlingar I Fysik, Kemii 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.


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

Fraternal Publications—The Chrome and Blue

One long-standing communication medium between the National Office and the subordinate chapters has been the monthly publication of The Chrome and Blue. The first issue was distributed in August 1927. Titled Monthly Report of the Grand Recorder, it was to be a confidential information exchange from Grand Recorder John Kuebler to the Grand Chapter. Unlike The HEXAGON, which contained information of broad interest to all members, the Monthly Report of the Grand Recorder was tightly focused on what was happening in the National Office. After the 1930 Conclave, the Office of the Grand Recorder modified its monthly report to be an informational resource to the collegiate chapters. At the suggestion of New England DC, Avery Ashdown, (Alpha Zeta), the reimagined publication was named The Chrome and Blue. After the new name went into effect, SC member Marion Dice frequently referred to it as The Chromium Blues. While The Chrome and Blue was issued by the National Office, it was expected that there would be other contributors. Supreme Council proposition 632, dated August 15, 1932, creating the Order of Altotus, listed among the duties of the Order was, "...to keep in touch with the Fraternity through The Chrome and Blue and The HEXAGON..." The first incarnation of The Chrome and Blue ceased publication with the December 1945 issue as both a cost cutting measure and a war-related resource shortage. During its summer meeting in 1957, the Supreme Council directed the Grand Recorder to resurrect The Chrome and Blue as a confidential monthly newsletter issued to the Supreme Council, District Counselors and the Order of Altotus. The re-launched publication began publication with the January 1958 issue. Collegiate Chapter MA's and Professional Chapter presidents were soon added to the distribution. The second version of The Chrome and Blue did not endure for long with the retirement of J. R. Kuebler, considerable personnel turnover in the National Office, and the appointment of a Grand Recorder that lived outside of Indianapolis. The Chrome and Blue became a casualty of too much to do and not enough staff to do it. But The Chrome and Blue was too good of an idea to stay dormant for too long. For the third time, Grand Recorder Jim Miller resumed publication of The Chrome and Blue. The première issue, dated September 1971, reset the counter and was distributed as Volume I, Number 1. The stated purpose of this third incarnation of the newsletter was to serve as a means of communication between the national officers and chapter officers, both collegiate and professional. The Chrome and Blue was to be mailed on the Friday of the last week of each month from September through May with each issue to contain a six-week calendar of all fraternity business, news items of interest to chapter officers and timely announcements from the Supreme Council and Grand Recorder.

For decades, The Chrome and Blue was a part of a monthly mailing that came to the chapters, recognizable by its printing on alternating blue and yellow pages. But mail is too slow a medium in a modern age, so in the fall of 2005, under GR Pat Johanns, The Chrome and Blue was no longer delivered via the U.S. Postal Service, but as a file saved in the Portable Document Format (pdf) and clickable on the National website. Gone were the blue and yellow pages, replaced with stock graphics and clickable links to other resources. Like the Fraternity itself, it has come a long way since its inception 88 years ago.

And as of fall 2015, The Chrome and Blue is once again being discontinued. The Fraternity is moving the distribution of its information to chapters through various social media outlets and the website.