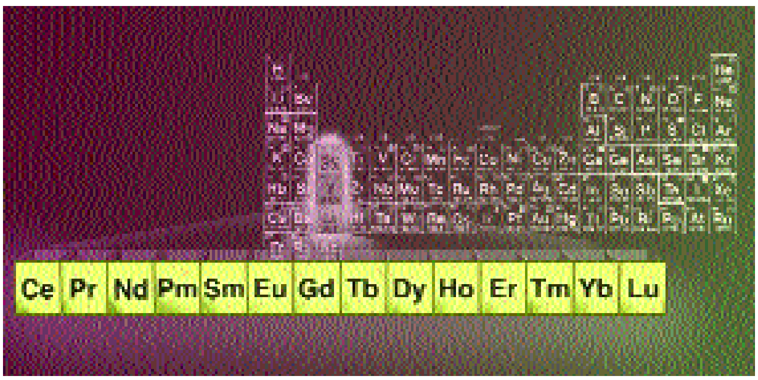
The Quietly Expanding Rare-Earth Market

Below the periodic table are two extra rows of elements that apparently could not be squeezed into the Russian chemist Dmitri Mendeleev's elegant summary of the material world. The top row, or series, is called the lanthanides, so named because the elements in it chemically resemble lanthanum, an element in the third column of the periodic table. Together with scandium and yttrium, which fall in the same column of the periodic table as lanthanum, these elements make up a group called the rare-earth elements.

Rare earths are late bloomers, commercially speaking. They were discovered in 1787, when Karl Axel Arrhenius, a lieutenant in the Swedish army, collected a rare-earth-bearing ore from a feldspar-and-quartz mine near the village of Ytterby, Sweden. The first application for rare earths was invented nearly 100 years later. (That was the Welsbach gas mantle: fabric impregnated with rare-earth salts, which when heated by a gas flame, gave off an intense white light.) It was not until this century that mixed rare earths began to see substantial commercial use and until the 1960s that purified oxides were in much demand. But over the last 20 years commercial applications have come on in leaps and bounds.



Lanthanide series of the periodic table.

Pete Krumhardt

A 3.6-kg can of pure dysprosium sells for $50,000.

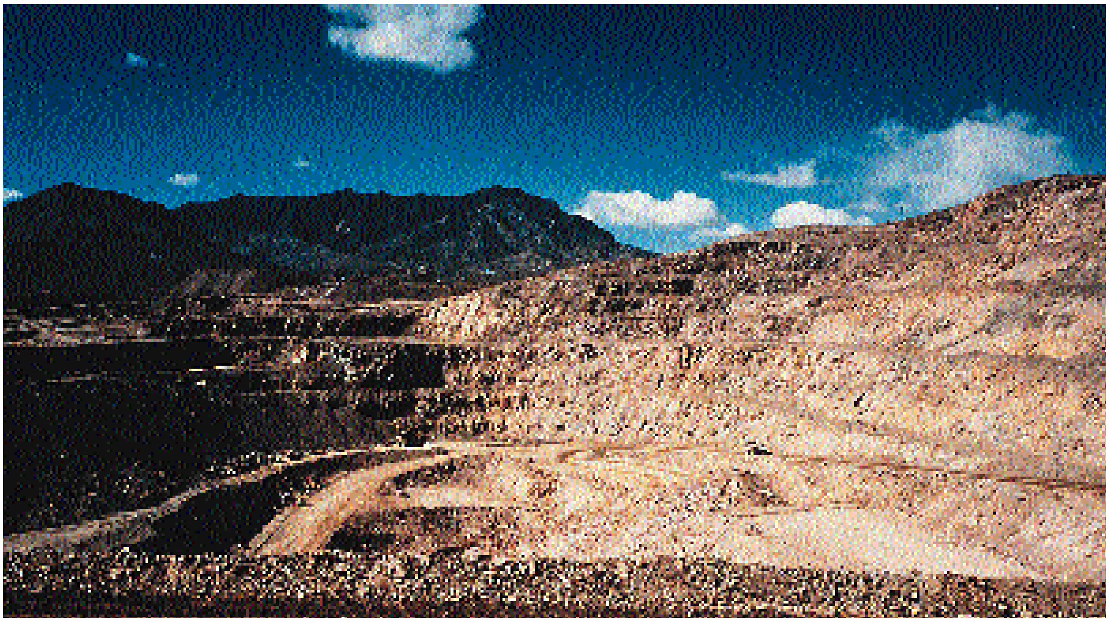
Advanced applications

According to *Rare Earths: Worldwide Markets, Applications, Technologies*—a book that costs only slightly less than a kilogram of purified thulium oxide ($2,750)—the total market for rare earths should reach a level of $568 million by 1999, reflecting an 8.1% annual growth rate. Most of the growth will come in applications for separated rare earths. According to the last mineral commodity summary on rare earths produced by the U.S. Bureau of Mines (before the bureau was eliminated by congressional fiat), "[D]emand for rare earths continues to shift towards higher purity mixed and separated products with applications in a wider range of products. This trend of increased demand and diversification is expected to accelerate through the year 2000."

The new, technologically sophisticated applications for rare earths typically exploit their magnetic or optical properties. Two of the most important permanent-magnet materials—namely neodymium-iron-boron and samarium-cobalt—include rare-earth elements. Both materials have magnetic strengths, as measured in terms of an "energy product," much greater than those of the more common alinco and ferrite permanent magnets. Many neodymium-iron-boron magnets can be found in cars, where they are used in various motors (starting, window, fan, and fuel pump) and in sensors, indicators, and controls. Another important market for the magnets is voice coil motors for computer disk drives. The drives would not be so small, respond so fast, or store as much data without rare-earth-based magnets.

Other applications exploit the magneto-optic or magnetostrictive effects in rare-earth elements or compounds. Rare-earth alloys such as terbium-iron-cobalt are used in magneto-optical storage systems, which can store 15 to 50 times more information than the conventional magnetic hard disk. Information is stored by using laser heating to induce a change in the direction of magnetization of magnetic domains in the magneto-optic medium. A material called Terfenol, an alloy of terbium, dysprosium, and iron, exhibits "giant" magnetostriction, expanding or contracting in an applied magnetic field and generating a magnetic pulse in response to a stress. Some uses of Terfenol include sonar devices, micropositioners, and liquid control valves.

The television industry has long been a heavy user of the rare earths. The sudden improvement of color TV images in the early 1960s was due to the replacement of the existing red phosphor, which could not be made to fluoresce as intensely as the green and blue phosphors, with a brilliant red phosphor consisting of europium oxide in a yttrium host. Cerium oxide is used as an antibrowning agent for the TV front plate,


Molycorp, Inc.

At this mine in Mountain Pass, California, a rich deposit of bastnasite is processed to recover and separate all the naturally occurring lanthanide elements and yttrium.

and cerium oxide is used to polish the front plate. A more recent optical application for rare earths is trichromatic fluorescent lamps. The lamps, which emit white light produced by mixing of three colors of light produced by rare-earth phosphors, are much more efficient than conventional fluorescent tubes.

The optical properties of the rare earths are also exploited in lasers and optical fibers. The most important application is the use of neodymium and yttrium in Nd:YAG (yttrium aluminum garnet) lasers, one of the most popular lasers in use today. The optimal transmission frequencies of fluoride glass optical fibers can be shifted by adding small amounts of rare-earth dopants. The doped fibers are used in fiberoptic sensors, infrared imagers and optical amplifiers, among other applications. For example, optical amplifiers can be made with erbium-doped optical fibers. First demonstrated in 1986, these devices allow the design of very long single-span optical fiber systems without intermediate repeaters or regenerators.

In some applications for rare earths the impetus is less economic than environmental. Rechargeable nickel metal-hydride batteries, which employ $LaNi_5$ as a hydrogen absorber, are replacing rechargeable batteries that contain cadmium, a toxic heavy metal. The catalytic converters that turn harmful automobile emissions into water, nitrogen, and carbon dioxide contain the rare earth cerium. And Rhône-Poulenc, Inc., a pharmaceuticals and chemicals company headquartered in Paris, has developed a new family of red pigments, including cerium sulfide, that can replace heavy-metal-based pigments used for coloring plastics and other materials.

Rare-earth properties

The delayed development of rare earths has to do with their distinctive chemical and physical properties. Although rare earths have different numbers of electrons, the variation occurs not in the outermost shells, as is generally the case, but in one of the inner shells—the 4f shell. All of the other shells, up to and including 5s and 5p, which are "outside" the 4f shell, are filled completely, but the 4f shell is open. The various rare earths are identified by the number of electrons they have in the 4f shell. The 4f shell has room for 14 electrons; lanthanum has no electrons in the 4f shell and lutetium has 14.

This electronic structure has two consequences. First, the outermost electrons primarily determine an element's chemical behavior and rare earths all have three outer electrons, so they are chemically very similar. Indeed, as one authority put it: "The fact that these elements have not been separated into minerals containing individual members of the family at any time in the Earth's history—even after eons of repeated melting and resolidifying, mountain formation and erosion, exposure to hot vapour, and immersion in seawater—attests to the great similarity in [their] properties..." Economical means of purifying rare earths were not invented until the 1940s, and even today the prices of pure rare-earth oxides reflect the difficulty of separating them. The word lanthanum is derived from the Greek *lanthanein*, which means hidden or concealed.

Second, this electron structure gives the rare earths the unusual optical and magnetic properties exploited by today's technologically sophisticated applications. Solid rare-earth elements and compounds have particularly sharp spectral lines, because transitions between different energy states of the 4f subshell are comparatively unaffected by the element's environment. Moreover, the magnetic effects of the different electrons in the incomplete 4f subshell do not cancel each other as they do in a completed subshell, giving rise to strong magnetism. Some rare-earth elements have saturation moments (the magnetism observed when all of the magnetic moments of the ions in the material are aligned) greater than those of iron, cobalt, and nickel.

The rare earths are neither particularly rare nor are they earths. (The early Greeks defined earths as materials that could not be changed further by heating. Until late in the 18th century the oxides of metals such as aluminum were known as earths and thought to be elements.) But the rare earths are ubiquitous, and present as subtle additives in many of the high-tech devices on which modern life depends.

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