Science > Chemistry

rare-earth element



Rare-earth element, any member of the group of chemical elements consisting of three elements in Group 3 (scandium [Sc], yttrium [Y], and lanthanum [La]) and the first extended row of elements below the main body of the periodic table (cerium [Ce] through lutetium [Lu]). The elements cerium through lutetium are called the

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<u>lanthanides</u>, but many scientists also, though incorrectly, call those elements rare earths.

The rare earths are generally trivalent elements, but a few have other <u>valences</u>. Cerium, <u>praseodymium</u>, and <u>terbium</u> can be tetravalent; <u>samarium</u>, <u>europium</u> and <u>ytterbium</u>, on the other hand, can be divalent. Many introductory <u>science</u> books view the rare earths as being so chemically similar to one another that collectively they can be considered as one element. To a certain degree that is correct—about 25 percent of their uses are based on this close similarity—but the other 75 percent of rare-earth usage is based on the unique properties of the individual elements. Furthermore, a close examination of these elements reveals vast differences in their behaviours and properties; e.g., the melting point of lanthanum, the

prototype element of the <u>lanthanide</u> series (918 °C, or 1,684 °F), is much lower than the melting point of lutetium, the last element in the series (1,663 °C, or 3,025 °F). This difference is much larger than that found in many groups of the periodic table; e.g., the melting points of <u>copper</u>, <u>silver</u>, and <u>gold</u> vary by only about 100 °C (180 °F).

The name *rare earths* itself is a misnomer. At the time of their discovery in the 18th century, they were found to be a component of complex oxides, which were called "earths" at that time. Furthermore, these <u>minerals</u> seemed to be <u>scarce</u>, and thus these newly discovered elements were named "rare earths." Actually, these elements are quite abundant and exist in many workable deposits throughout the world. The 16 naturally occurring rare earths fall into the 50th percentile of elemental abundances. By the early 21st century, <u>China</u> had become the world's largest producer of rare-earth elements. <u>Australia</u>, <u>Brazil</u>, <u>India</u>, Kazakhstan, <u>Malaysia</u>, <u>Russia</u>, <u>South Africa</u>, and the <u>United States</u> also extract and refine significant quantities of these materials.

Many people do not realize the enormous impact the rare-earth elements have on their daily lives, but it is almost impossible to avoid a piece of modern technology that does not contain any. Even a product as simple as a lighter flint contains rareearth elements. Their pervasiveness is exemplified by the modern automobile, one of the biggest consumers of rare-earth products. Dozens of electric motors in a typical automobile, as well as the speakers of its sound system, use neodymiumiron-boron permanent magnets. Electrical sensors employ yttria-stabilized zirconia to measure and control the <u>oxygen</u> content of the fuel. The three-way <u>catalytic</u> converter relies on cerium oxides to reduce <u>nitrogen</u> oxides to nitrogen gas and oxidize carbon monoxide to carbon dioxide and unburned hydrocarbons to carbon dioxide and water in the exhaust products. Phosphors in optical displays contain yttrium, europium, and terbium oxides. The windshield, mirrors, and lenses are polished using cerium oxides. Even the gasoline or diesel fuel that propels the vehicle was refined using rare-earth cracking catalysts containing lanthanum, cerium, or mixed-rare-earth oxides. Hybrid automobiles are powered by a <u>nickel</u>lanthanum metal hydride rechargeable battery and an electrical traction motor, with permanent magnets containing rare-earth elements. In addition, modern

media and communication devices—cell phones, televisions, and computers—all employ rare earths as magnets for speakers and hard drives and phosphors for optical displays. The amounts of rare earths used are quite small (0.1–5 percent by weight, except for permanent magnets, which contain about 25 percent neodymium), but they are critical, and any of those devices would not work as well, or would be significantly heavier, if it were not for the rare earths.

Discovery and history

Although the rare earths have been around since the formation of <u>Earth</u>, their existence did not come to light until the late 18th century. In 1787 the Swedish army lieutenant Carl Axel Arrhenius discovered a <u>unique</u> black <u>mineral</u> in a small quarry in Ytterby (a small town near Stockholm). That mineral was a mixture of rare earths, and the first individual <u>element</u> to be isolated was <u>cerium</u> in 1803.



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The history of the individual rare-earth elements is both complex and confused, mainly because of their chemical similarity. Many "newly discovered elements" were not one element but mixtures of as many as six different rare-earth elements. Furthermore, there were claims of discovery of a large number of other "elements," which were supposed to be members of the rare-earth series but were not.

The last naturally occurring rare-earth element (<u>lutetium</u>) was discovered in 1907, but research into the <u>chemistry</u> of these elements was difficult because no one knew how many true rare-earth elements existed. Fortunately, in 1913–14 the research of Danish physicist <u>Niels Bohr</u> and English physicist <u>Henry Gwyn Jeffreys Moseley</u> resolved this situation. <u>Bohr's theory of the hydrogen atom</u> enabled theoreticians to show that only 14 <u>lanthanides</u> exist. Moseley's experimental studies <u>verified</u> the existence of 13 of these elements and showed that the 14th lanthanide must be element 61 and lie between <u>neodymium</u> and <u>samarium</u>.

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In the 1920s the search for element 61 was intense. In 1926 groups of scientists at the <u>University of Florence</u>, Italy, and at the <u>University of Illinois</u> claimed to have discovered element 61 and named the element florentium and illinium, respectively, but their claims could not be independently verified. The furor of these claims and counterclaims eventually died down by 1930. It was not until 1947, after the <u>fission</u> of <u>uranium</u>, that element 61 definitely was isolated and named <u>promethium</u> by scientists at the U.S. <u>Atomic Energy Commission</u>'s <u>Oak Ridge</u> National Laboratory in Tennessee. (More details about the discovery of the individual elements are found in the articles about those elements.)

During the 160 years of discovery (1787–1947), the <u>separation and purification</u> of the rare-earth elements was a difficult and time-consuming process. Many scientists spent their whole lives attempting to obtain a 99 percent pure rare earth, usually by <u>fractional</u> crystallization, which makes use of the slight differences of the <u>solubility</u> of a rare-earth salt in an aqueous <u>solution</u> compared with that of a neighbouring <u>lanthanide</u> element.

Because the rare-earth elements were found to be <u>fission products</u> of the splitting of a uranium atom, the U.S. Atomic Energy <u>Commission</u> made a great effort to develop new methods for separating the rare-earth elements. However, in 1947 Gerald E. Boyd and colleagues at Oak Ridge National Laboratory and <u>Frank Harold Spedding</u> and colleagues at the Ames Laboratory in Iowa simultaneously published results which showed that <u>ion</u>-exchange processes offered a much better way for separating the rare earths.

Abundance, occurrence, and reserves

As noted above, the rare earths are fairly abundant, but their availability is somewhat limited, primarily because their concentration levels in many ores are quite low (less than 5 percent by weight). An economically viable source should

contain more than 5 percent rare earths, unless they are mined with another product—e.g., <u>zirconium</u>, <u>uranium</u>, or <u>iron</u>—which allows economic recovery of <u>ore</u> bodies with concentrations of as little as 0.5 percent by weight.

Of the 83 naturally occurring elements, the 16 naturally occurring rare-earth elements fall into the 50th percentile of the elemental abundances. Promethium, which is radioactive, with the most stable isotope having a half-life of 17.7 years, is not considered to be naturally occurring, although trace amounts have been found in some radioactive ores. Cerium, which is the most abundant, ranks 28th, and thulium, the least abundant, ranks 63rd. Collectively, the rare earths rank as the 22nd most abundant "element" (at the 68th percentile mark). The non-lanthanide rare-earth elements, yttrium and scandium, are 29th and 44th, respectively, in their abundances.

Lanthanum and the light lanthanides (cerium through <u>europium</u>) are more abundant than the heavy lanthanides (<u>gadolinium</u> through <u>lutetium</u>). Thus, the individual light lanthanide elements are generally less expensive than the heavy lanthanide elements. Furthermore, the metals with even <u>atomic numbers</u> (cerium, <u>neodymium</u>, <u>samarium</u>, gadolinium, <u>dysprosium</u>, <u>erbium</u>, and <u>ytterbium</u>) are more abundant than their neighbours with odd atomic numbers (lanthanum, <u>praseodymium</u>, promethium, europium, <u>terbium</u>, <u>holmium</u>, thulium, and lutetium).

Rare-earth ore deposits are found all over the world. The major ores are in <u>China</u>, the <u>United States</u>, <u>Australia</u>, and <u>Russia</u>, while other <u>viable</u> ore bodies are found in <u>Canada</u>, <u>India</u>, <u>South Africa</u>, and southeast Asia. The major minerals contained in these ore bodies are <u>bastnasite</u> (fluorocarbonate), <u>monazite</u> (<u>phosphate</u>), <u>loparite</u> $[(R,Na,Sr,Ca)(Ti,Nb,Ta,Fe^{3+})O_3]$, and <u>laterite</u> clays $(SiO_2,Al_2O_3,andFe_2O_3)$.

Chinese deposits accounted for about 80 percent of the rare earths mined in the world in 2017 (105,000 tons of rare-earth oxide). About 94 percent of the rare earths mined in China are from bastnasite deposits. The major deposit is located at Bayan Obo, Inner Mongolia (83 percent), while smaller deposits are mined in Shandong (8 percent) and Sichuan (3 percent) provinces. About 3 percent comes from laterite (ion absorption) clays located in Jiangxi and Guangdong provinces in

southern China, while the remaining 3 percent is produced at a variety of locations.

Officially, 130,000 metric tons of REO equivalent was mined in 2017, but a <u>black</u> market in rare earths was said to produce an additional 25 percent of that amount. Most black-market rare-earth materials are smuggled out of China.

China's monopoly allowed it to raise prices by hundreds of percent for various rare-earth materials from 2009 to 2011 and also to impose export quotas on many of these products. This brought about a large change in the dynamics of the rare-earth markets. Mining of bastnasite resumed at Mountain Pass, California, in 2011 after a nine-year hiatus, and mining of monazite began that same year at Mount Weld, Australia. At the same time, loparite was being mined in Russia, while monazite was mined in India, Vietnam, Thailand, and Malaysia. Those and other mining operations brought a new equilibrium between demand and supply in which China was still the major supplier of rare-earth minerals, but companies either sought alternative sources, used less, or recycled more rare earths.

As of 2017, known world reserves of rare-earth minerals amounted to some 120 million metric tons of contained REO. China has the largest fraction (37 percent), followed by Brazil and Vietnam (18 percent each), Russia (15 percent), and the remaining countries (12 percent). With reserves this large, the world would not run out of rare earths for more than 900 years if demand for the minerals would remain at 2017 levels. Historically, however, demand for rare earths has risen at a rate of about 10 percent per year. If demand continued to grow at this rate and no recycling of produced rare earths were undertaken, known world reserves likely would be exhausted sometime after the mid-21st century.

Considering both the limited reserves and high value of the rare-earth <u>metals</u>, recycling these elements from consumer products that reach the end of their useful life is expected to become more important. At present, only <u>scrap metal</u>, <u>magnet</u> materials, and <u>compounds</u> used in the manufacture of <u>phosphors</u> and <u>catalysts</u> are recycled. However, products that contain relatively large amounts of rare earths could be recycled immediately using existing techniques. These include rechargeable <u>nickel-metal</u> hydride batteries that contain a few grams to a few kilograms of LaNi₅-based <u>alloys</u> as a <u>hydrogen</u> absorber as well as large SmCo₅-

and Nd₂Fe₁₄B-based permanent magnets. All of these materials hold 25-30 percent by weight light lanthanides—much more than even the best rare-earthcontaining ore (see below). However, the majority of consumer electronic devices contain only small amounts of rare earths. For example, a hard drive's spindle magnet contains only a few grams of Nd₂Fe₁₄B. A speaker magnet of a cellular phone makes up less than 0.1 percent of the total mass of the telephone. A compact fluorescent lamp has only a fraction of a gram of lanthanide metals in the phosphor. Considering the complexity of many modern electronic devices, recycling of rare earths must be done simultaneously with recycling of other valuable resources and potentially dangerous substances. These include precious metals (such as silver, gold, and palladium), nonferrous metals (such as aluminum, cobalt, nickel, copper, gallium, and zinc), carcinogens (such as cadmium), poisons (such as mercury, lead, and beryllium), plastics, glass, and ceramics. Numerous scientific and engineering issues, therefore, must be resolved, first, in order to create consumer products that are easily recyclable at the end of their life and, second, to make recycling of rare earths both meaningful and economical, thus making the best use of the rare earths—an extremely valuable but limited resource provided by nature.

Minerals and ores

The content of the individual rare-earth <u>elements</u> varies considerably from <u>mineral</u> to mineral and from deposit to deposit. The minerals and ores are generally classified as "light" or "heavy"; in the former <u>group</u> most of the elements present are the light-<u>atomic-weight</u> elements (i.e., <u>lanthanum</u>, <u>cerium</u>, <u>praseodymium</u>, <u>neodymium</u>, <u>samarium</u>, and <u>europium</u>), whereas most of the elements in the latter group are the heavy-atomic-weight elements (i.e., <u>gadolinium</u>, <u>terbium</u>, <u>dysprosium</u>, <u>holmium</u>, <u>erbium</u>, <u>thulium</u>, <u>ytterbium</u>, and <u>lutetium</u>, plus <u>yttrium</u>, which is considered to be a member of the heavy group because it is found in the ores with the heavy lanthanides). The <u>geochemistry</u> of <u>scandium</u> is significantly different from the geochemistry of the other rare-earth elements. Information on its ores and minerals is provided in the article <u>scandium</u>. Essentially no scandium is found in any of the minerals discussed below.

Of the approximately 160 minerals that are known to contain rare earths, only four are currently mined for their rare earths: bastnasite, laterite clays, monazite, and loparite. With the exception of laterite clays, these minerals are good sources of light lanthanides and lanthanum and account for about 95 percent of the rare earths in use. Laterite clays are a commercial source of the heavy lanthanides and yttrium.

Other minerals that have been used as a source of rare earths are <u>apatite</u>, <u>euxenite</u>, gadolinite, and <u>xenotime</u>. Allanite, <u>fluorite</u>, <u>perovskite</u>, sphene, and <u>zircon</u> have the potential to be future sources of rare earths. (In addition, <u>uranium</u> and <u>iron</u> tailings have been used in the past as a source of the heavy lanthanides plus yttrium and of the light lanthanides plus lanthanum, respectively.) Many of these minerals such as apatite and euxenite are processed for other <u>constituents</u>, and the rare earths could be extracted as a by-product. In addition to minerals found in Earth's crust, there are some deep-sea muds, such as those near <u>Minamitori Island</u>, Japan, that contain rare-earth elements. The concentrations vary from hundreds to thousands of parts per million, and these muds may one day be a source of rare earths.

The idealized chemical <u>compositions</u> of these 13 minerals that are sources of rare earths are given in the table.

| Composition of selected rare-earth minerals | | | | | |
|---|--|---------------------------------------|--|--|--|
| name | idealized composition | primary rare-earth content | | | |
| allanite | $(Ca,Fe^{2+})(R,AI,Fe^{3+})_3Si_3O_{13}H$ | R = light lanthanoids | | | |
| apatite | Ca ₅ (PO ₄) ₃ F | R = light lanthanoids | | | |
| bastnasite | RCO ₃ F | R = light lanthanoids (60–70%) | | | |
| euxenite | R(Nb,Ta)TiO ₆ · xH ₂ O | R = heavy lanthanoids plus Y (15–43%) | | | |
| fluorite | CaF ₂ | R = heavy lanthanoids plus Y | | | |
| gadolinite | $R_2(Fe^{2+},Be)_3Si_2O_{10}$ | R = heavy lanthanoids plus Y (34–65%) | | | |
| laterite clays | SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ | R = heavy lanthanoids plus Y | | | |

| loparite | (R,Na,Sr,Ca)(Ti,Nb,Ta,Fe ³⁺)O ₃ | R = light lanthanoids (32–34%) | |
|------------|--|---|--|
| monazite | RPO ₄ | R = light lanthanoids (50–78%) | |
| perovskite | CaTiO ₃ | R = light lanthanoids | |
| sphene | CaTiSiO ₄ X ₂ (X = $\frac{1}{2}$ O ²⁻ , OH ⁻ , or F ⁻) | R = light lanthanoids | |
| xenotime | RPO ₄ | R = heavy lanthanoids plus Y (54–65%) | |
| zircon | ZrSiO ₂ | R = both light and heavy lanthanoids plus Y | |

Bastnasite

Bastnasite, a fluorocarbonate, is the principal source of rare earths. About 94 percent of the rare earths used in the world come from mines in Mountain Pass, California, U.S.; Bayan Obo, Inner Mongolia, China; Shandong province, China; and Sichuan province, China. The Bayan Obo deposit is slightly richer in praseodymium and neodymium than the Mountain Pass bastnasite is, primarily at the expense of the lanthanum content, which is 10 percent greater in the Mountain Pass ore. The rare-earth contents of the Shandong and Sichuan minerals are slightly different from that of the Bayan Obo minerals and also from each other's. The Shandong bastnasite is similar to the Mountain Pass mineral. The Sichuan ore has more lanthanum, less praseodymium and neodymium, and about the same amount of cerium as the Bayan Obo deposit.



The rare-earth content in selected minerals, including some bastnasites, is given in the table.

| Rare-earth content in selected minerals (%) | | | | | | | |
|---|----------------------------------|--|-----------------------------|----------------------------------|---|--|---|
| rare- earth element | bastnasite (Mountain Pass, | bastnasite (Bayan Obo, China) | monazite (Mount Weld, | xenotime (Lehat, Malaysia) | high-Y laterite (Longnan, China) | low-Y laterite (Xunwu, China) | loparite (Kola Peninsula Russia) |

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|----|---------------|-------------|------------|-------|------|---------|----------|
| La | 33.8 | 23.0 | 25.5 | 1.2 | 1.8 | 43.4 | 25.0 |
| Ce | 49.6 | 50.0 | 46.7 | 3.1 | 0.4 | 2.4 | 50.5 |
| Pr | 4.1 | 6.2 | 5.3 | 0.5 | 0.7 | 9.0 | 5.0 |
| Nd | 11.2 | 18.5 | 18.5 | 1.6 | 3.0 | 31.7 | 15.0 |
| Sm | 0.9 | 0.8 | 2.3 | 1.1 | 2.8 | 3.9 | 0.7 |
| Eu | 0.1 | 0.2 | 0.4 | trace | 0.1 | 0.5 | 0.1 |
| Gd | 0.2 | 0.7 | <0.1 | 3.5 | 6.9 | 3.0 | 0.6 |
| Tb | 0.0 | 0.1 | <0.1 | 0.9 | 1.3 | trace | trace |
| Dy | 0.0 | 0.1 | 0.1 | 8.3 | 6.7 | trace | 0.6 |
| Но | 0.0 | trace | trace | 2.0 | 1.6 | trace | 0.7 |
| Er | 0.0 | trace | trace | 6.4 | 4.9 | trace | 0.8 |
| Tm | 0.0 | trace | none | 1.1 | 0.7 | trace | 0.1 |
| Yb | 0.0 | trace | none | 6.8 | 2.5 | 0.3 | 0.2 |
| Lu | trace | trace | none | 1.0 | 0.4 | 0.1 | 0.2 |
| Y | 0.1 | trace | <0.1 | 61.0 | 65.0 | 8.0 | 1.3 |

Laterite clays

The laterite clays (also known as ion-absorption clays) are primarily composed of silica, alumina, and ferric oxide; those that also contain <u>viable</u> amounts of rare earths are found only in <u>Jiangxi</u> province of southeast China. Of the Jiangxi deposits, the clays located near Longnan are quite rich in the heavy lanthanides and yttrium. The clays at Xunwu have a most unusual distribution of rare earths, being rich in lanthanum and neodymium with a reasonably high yttrium content. The low concentrations of cerium and praseodymium in both clays, especially in the Xunwu <u>clay</u>, compared with the normal rare-earth distribution in the other minerals, is also remarkable. These clays are the main source of heavy elements used in rare-earth-containing products—e.g., <u>dysprosium</u> in Nd₂Fe₁₄B permanent <u>magnets</u>.

Monazite

Monazite, a phosphate, is the third most important ore source of rare earths. In the 1980s it accounted for 40 percent of the world's production, but by 2010 it contributed only a small fraction to the mined rare earths. There were two reasons for this change: first, it is more costly to process monazite from the ore body to a rare-earth concentrate than to process bastnasite; second, monazite contains a significant amount of radioactive thorium dioxide (ThO₂) compared with bastnasite, and thus special environmental procedures in handling and storage are needed. However, monazite is expected to contribute a growing share of mined rare earths as operations at Mount Weld, Australia, are brought up to full production by the end of 2014.

Monazite is widely distributed; in addition to Australia, it is found in <u>India</u>, <u>Brazil</u>, <u>Malaysia</u>, countries of the <u>Commonwealth of Independent States</u>, the <u>United</u> <u>States</u>, Thailand, <u>Sri Lanka</u>, the <u>Democratic Republic of the Congo</u>, <u>South Korea</u>, and <u>South Africa</u>.

Loparite

Loparite is a complex mineral that is mined primarily for its <u>titanium</u>, <u>niobium</u>, and <u>tantalum</u> content, with the rare earths extracted from the ore as a by-product. This ore is found mainly in the <u>Kola Peninsula</u> in northwest <u>Russia</u> and in Paraguay. Its rare-earth distribution is similar to that of bastnasite, except it has significantly higher concentrations of the heavy lanthanides and yttrium.

Xenotime

Xenotime is a <u>phosphate mineral</u>, similar to monazite except enriched in the heavy lanthanides and yttrium. It has been mined for many years but has contributed only about 1 percent of the total rare earths mined since the 1970s. Xenotime contains smaller amounts of the radioactive <u>compounds</u> U_3Q_8 and ThO_2 than monazite. Because of its high concentrations of yttrium and heavy lanthanides, xenotime is used as a source material for the individual rare-earth elements rather than being used as a mixture of heavy rare earths. The major producer of xenotime

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Electronic structure and ionic radius

The chemical, <u>metallurgical</u>, and physical behaviours of the rare earths are governed by the <u>electron configuration</u> of these elements. In general, these elements are

Electron probabilities, $P^2(r)$, for the 4f, 5s, 5p, 5d, and 6s electrons of gadolinium.

trivalent, R^{3+} , but several of them have other <u>valences</u>. The number of 4f <u>electrons</u> of each <u>lanthanide</u> is given in the table of the number of 4f electrons and ionic radii for the R^{3+} <u>ion</u>. The 4f electrons have lower energies than and radially lie inside the outer three valence electrons (i.e., 4f electrons are "localized" and part of the ion core), and thus they do not directly participate in the bonding with other elements when a <u>compound</u> is formed. This is why the lanthanides are chemically similar and difficult to separate and why they occur together in various minerals. The outer or valence electrons for the 14 lanthanides and lanthanum are the same, $5d6s^2$; for <u>scandium</u>, $3d4s^2$; and for <u>yttrium</u>, $4d5s^2$. There is some variation in the chemical properties of the lanthanides because of the <u>lanthanide contraction</u> and the hybridization, or mixing, of the 4f electrons with the valence electrons.

The <u>systematic</u> and smooth decrease from <u>lanthanum</u> to <u>lutetium</u> is known as the lanthanide contraction. It is due to the increase in the nuclear charge, which is not completely screened by the additional 4*f* electron as one goes from one lanthanide to the next. This increased effective charge draws the electrons (both the core and outer valence electrons) closer to the nucleus, thus accounting for the smaller radius of the higher-<u>atomic-number</u> lanthanides. The lanthanide contraction also accounts for the decreased basicity from lanthanum to <u>lutetium</u> and is the basis of various separation techniques.

As the 4f electrons are added when one moves across the lanthanide series from lanthanum to <u>cerium</u> to <u>praseodymium</u> and so on, the electrons, which have a magnetic moment due to the electron's <u>spin</u>, maintain the same spin direction and the moments are aligned parallel with one another until the 4f level is half-filled—i.e., at seven 4f electrons in <u>gadolinium</u>. The next electron must align antiparallel in accordance with the <u>Pauli exclusion principle</u>, and thus two 4f electrons are

paired. This continues until the 14th electron is added at lutetium, where all the 4f electron spins are paired up, and lutetium has no 4f magnetic moment.

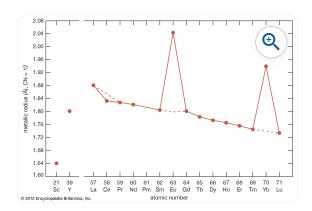
The 4*f* electron configuration is extremely important and determines the magnetic and optical behaviours for the lanthanide elements; e.g., the peculiar properties of strong Nd₂Fe₁₄B permanent <u>magnets</u> are due to the three 4*f* electrons in <u>neodymium</u>, and the red colour in optical displays that use cathode-ray tubes is provided by the <u>europium ion</u> in a host <u>compound</u>, while the green colour is provided by <u>terbium</u>.

As noted above, several lanthanides may exhibit another <u>valence</u> state, R^{4+} for R =cerium, praseodymium, and terbium and R^{2+} for R =samarium, europium, and ytterbium. These additional valence states are a striking example of Hund's rule, which states that empty, half-filled, and completely filled electronic levels tend to be more stable states: Ce^{4+} and Tb^{4+} give up an f electron to have an empty and half-filled 4f level, respectively, and Eu²⁺ and Yb²⁺ gain an f electron to have a half-filled or completely filled 4f level, respectively. Pr4+ and Sm2+ can, by giving up or gaining an f electron, respectively, in rare instances gain extra stability. In these two cases they tend toward but do not reach the respective empty or halffilled level. By giving up a 4f electron to become an \mathbb{R}^{4+} ion, the radii of cerium, praseodymium, and terbium become smaller, 0.80, 0.78, and 0.76 Å, respectively. Conversely, samarium, europium, and ytterbium gain a 4f electron from the valence electrons to become an R²⁺ ion, and their radii increase to 1.19, 1.17, and 1.00 Å, respectively. Chemists have made use of these valence changes to separate Ce⁴⁺, Eu²⁺, and Yb²⁺ from the other trivalent R³ ions by relatively cheap chemical methods. CeO₂ (where Ce is tetravalent) is the normal stable oxide form, while the oxides of praseodymium and terbium have the Pr₆O₁₁ and Tb₄O₇ stoichiometries containing both the tetra- and the trivalent states—i.e., $4 PrO_2 \cdot Pr_2O_3$ and ${
m 2TbO_2 \cdot Tb_2O_3}$, respectively. The divalent ions ${
m Sm^{2+}}$, ${
m Eu^{2+}}$, and ${
m Tb^{2+}}$ form dihalides -e.g., SmCl₂, EuCl₂, and YbCl₂. Several europium oxide stoichiometries are known: EuO (Eu²⁺), Eu₂O₃ (Eu³⁺), and Eu₃O₄ (i.e., EuO·Eu₂O₃).

The ionic radius of scandium is much smaller than that of the smallest lanthanide,

lutetium: 0.745 Å versus 0.861 Å. Scandium's radius is slightly larger than those of the common metal ions—e.g., Fe³⁺, Nb⁵⁺, U⁵⁺, and W⁵⁺. This is the main reason why scandium is essentially absent from any of the normal rare-earth minerals, generally less than 0.01 percent by weight. However, scandium is obtained as a byproduct of processing other ores (e.g., wolframite) and from mining tailings (e.g., uranium). On the other hand, the radius of yttrium, 0.9 Å, is nearly the same as that of holmium, 0.901 Å, and this accounts for the presence of yttrium in the heavy lanthanide minerals.

Most rare-earth metals have a valence of three; however, that of cerium is 3.2, and europium and <u>ytterbium</u> are divalent. This is quite evident when the metallic radii are plotted versus <u>atomic number</u>. The metallic radii of the trivalent metals exhibit the normal lanthanide contraction, but a noticeable deviation occurs for cerium, where its radius falls below the line established by the trivalent metals, and also

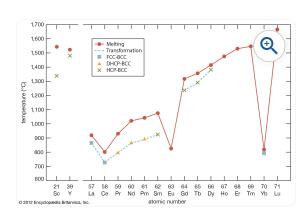


metallic radii Metallic radii of the rare-earth metals for a coordination number of 12 versus atomic number.

for europium and ytterbium, where their radii lie well above this line.

The melting points for europium and ytterbium are significantly lower than those of the neighbouring trivalent lanthanides when they are plotted versus atomic number, and this is also consistent with the divalent nature of these two metals.

Anomalies are also evident in other physical properties of europium and ytterbium compared with the trivalent lanthanide metals (see below Properties of the metals).



melting points and transformation temperatures Melting points and transformation temperatures of rare- ϵ ...(more)

The table presents the number of 4f electrons and the radius of the R^{3+} ion for the rare-earth elements.

Number of 4f electrons and ionic radii for the R³⁺ ion

| rare-earth element | number of 4f electrons | number of unpaired 4f electrons | ionic radius (Å) |
|-----------------------|------------------------|---------------------------------------|------------------------|
| La | 0 | 0 | 1.045 |
| Се | 1 | 1 | 1.01 |
| Pr | 2 | 2 | 0.997 |
| Nd | 3 | 3 | 0.983 |
| Pm | 4 | 4 | 0.97 |
| Sm | 5 | 5 | 0.958 |
| Eu | 6 | 6 | 0.947 |
| Gd | 7 | 7 | 0.938 |
| Tb | 8 | 6 | 0.923 |
| Dy | 9 | 5 | 0.912 |
| Но | 10 | 4 | 0.901 |
| Er | 11 | 3 | 0.890 |
| Tm | 12 | 2 | 0.880 |
| Yb | 13 | 1 | 0.868 |
| Lu | 14 | 0 | 0.861 |
| Sc | 0 | 0 | 0.745 |
| Y | 0 | 0 | 0.900 |