Rare Earths: Not Rare, But Everywhere

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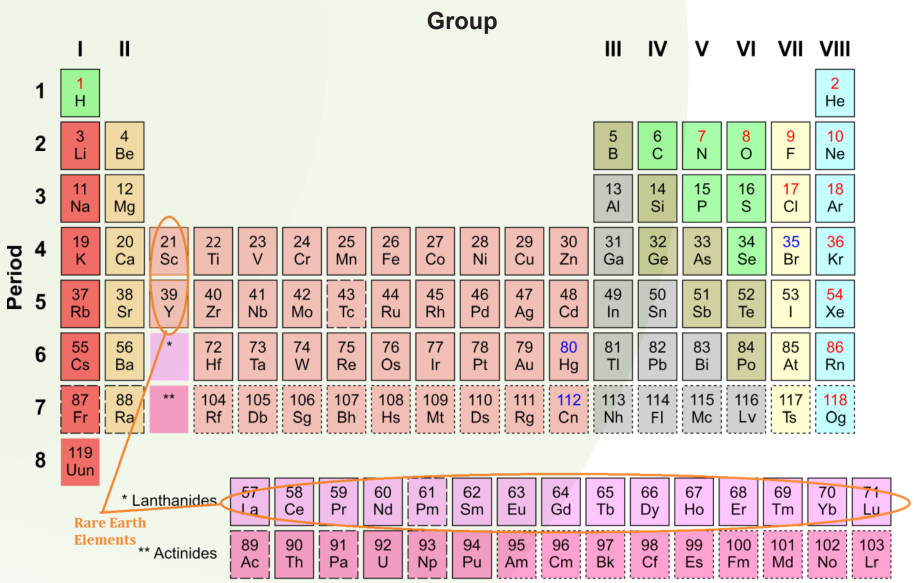


THE Periodic Table is a systematic arrangement of the chemical elements in rows and columns based on a scientific logic. The horizontal lines are called Periods wherein the atomic number of the elements increases by one from left to right. After the last element, the next number comes first in the next row and so on. The vertical columns so produced are called Groups.

As the atomic number also indicates the number of electrons in the atom's orbit, the thinkers could make a format of the Periodic Table such that the elements with the same valence come under each other in the same group. In other words, the chemical properties of the elements in a particular group are similar. In an arrangement like this it is axiomatic that one element lies at the intersection of a group and a period.

However, there are two strange exceptions in the third group (III A). In the third place in the 6^{th} and 7^{th} period, not one but a bunch of elements are found. Atomic numbers 57 to 71 in sixth the period are called Lanthanides behind element lanthanum, and numbers 89 to 103 are called Actinides after actinium (atomic no. 89). Lanthanides along with Scandium (Sc, 21) and Yttrium (Y, 39) are also called the Rare Earths.

They are not as rare as the name would suggest. On the contrary their utility is in wide variety of applications. If they were to disappear from the scene, all the glowing screens in our modern life (television, desktop computer, laptop, mobile phones, X-ray apparatus, etc.) would go colourless or even fade away. Automobiles on the roads would begin to emit toxic gases through their exhausts. Hard drives in computers would screech to a halt. Some nuclear reactors would not be able to shut down in emergency.

In recent years, due to the supply of these rare elements shrinking because of political reasons and the spread of applications increasing, they have attracted global attention. This is unsettling because it affects the environment friendly applications.

Discovery and Recovery

As they exhibit similar chemical behaviur it is natural that many of them occur together in nature, in the same or similar mineral deposits. However, the knowledge that they are a family came only after Bohr's atom model and subsequent work by Moseley and Urbain (See SR May 2019), which also gave them a definite place in the periodic table.

Their existence was first noticed in 1787 A.D. when C.A. Arrhenius found a black mineral in a quarry in Sweden at a place called Ytterby (names of three rare earths came from this town). The important minerals are bastnasite, monazite, xenotime and loparite. Lesser amounts are also found in zircon, euxenite, allanite and some kinds of clays. Bastnasite contains 98% of the lighter rare earths (Cerics); monazites are a by-product of Ilmenite, an ore for titanium. So is xenotime which is a better source for heavier rare earths (Yttrices). Promethimium (*Pr*) is one exception which was not found in nature, in any mineral because it is radioactive with a half life of only 12 years. After nuclear reactors came into existence, it was found in fission products.

The discovery of rare earth elements has spanned over a century because their separation was not easy. The journey was long and confused due to mixed identities.

Applications

Their applications fall in two broad categories; one where a group of rare earth elements or more than one element is used. The other where a specific element exclusively based on its properties is required, like Nd in magnets or Gd in nuclear reactors. The former includes catalysts, alloy making, colour pigments, etc.

Catalysts: Quantitatively this application is the largest and accounts for 60% of rare earth usage. Refineries use them in fuel cracking columns to conserve zeolite. La and Ce are used to prevent de-aluminization of zeolite and increase its life. This the increases yield of petrol and provides stability to the process. Of late new alternatives to REs are being developed due to the sudden rise in prices. Cerium is also used as a catalyst in catalytic convertersof automobiles, to control exhaust gas emissions like carbon monoxide and nitrogen oxides.

Glass Industry: The second most popular use of REs is in glass industry. They are used as additives in making of special glasses like ultraviolet resistant glass and photo optical glasses. In addition, oxides of cerium and lanthanum are used in polishing of glasses due to their hardness. La is used to provide anti-glare properties to the lenses used in optical instruments. Praseodimium is used in making wisers i.e. glass shields used during welding and glass blowing work.

Magnets: About 10% of the RE materials produced go in making magnets. Modern applications using permanent magnets are such that require strong magnetic field in smaller volumes, for example, disk drives and hard drives of computers. MRI machines for medical imaging and wind turbines also use magnets and that too large ones. Magnets for wind turbines can weigh over a ton. The next prospective demand is in motors for hybrid electric cars. Gadolinium is a good magnetic material but its abundance is lower than Nd and hence its use is in small-size magnets, as in computer memories.

Phosphors: This is the age of displays. Cathode ray tubes, sonography images,

Table 1: Rare earth elements and their discoverers

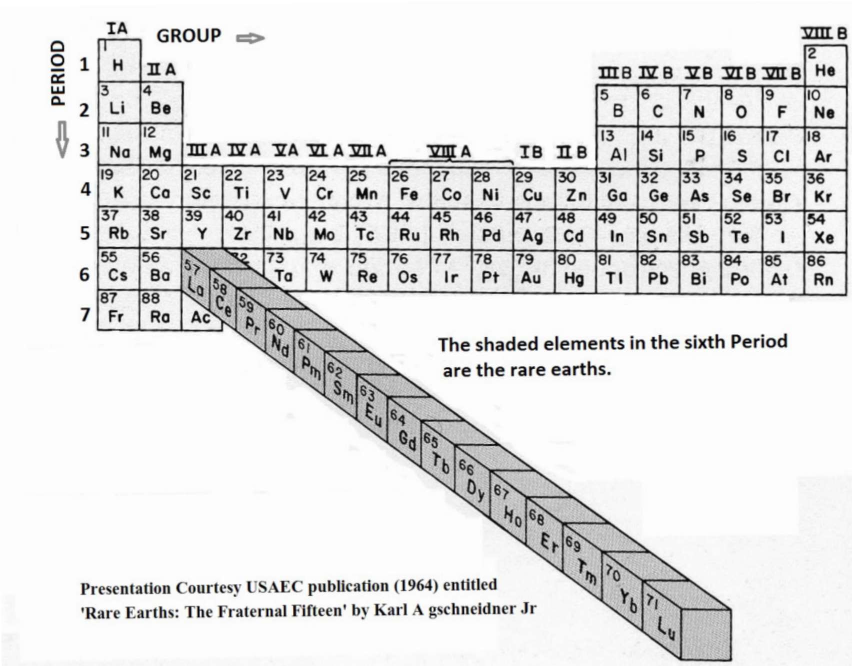
Atomic No.	Name of RE	Symbol	Discovered by	Year
57	Lanthanum	La	CG Mosander	1839
58	Cerium	Ce	MH Claproth JJ Berzelius W Hisinger	1803
59 60	Praseodymium Neodymium	Pr Nd	CA von Welsbach	1885
61	Promethium	Pm	JA Marinsky LE Glendenin CD Coryell	1947
62	Samarium	Sm	Lecoq de Boisbaudran	1879
63	Europium	Eu	William Crookes	1889
64	Gadolinium	Gd	JCG Marignac	1880
65	Terbium	Tb	CG Mosander	1843
66	Dysprosium	Dy	Lecoq de Boisbaudran	1886
67	Holmium	Ho	P T Cleve JL Soret	1879
68	Erbium	Er	CG Mosander	1843
69	Thulium	Tm	P T Cleve	1879
70	Ytterbium	Yb	JCG Marignac	1878
71	Lutetium	Lu	G Urbain CA von Welsbach	1907 1908

Note: Elements *La* to *Gd* are called lighter rare earths or Cerics and Tb to Lu are called heavy rare earths or Yttrices

Ref: *Rare Earths: The Fraternal Fifteen*, Karl A Gschneidner Jr, Published by US Atomic Energy Commission, 1964

medical and industrial X-ray pictures (including angiography), computer monitors, televisions and mobile phones – all have monochrome or coloured displays. Phosphors are the materials that make this possible. They glow (emit light) under different stimuli like electrical voltage, X-ray or gamma ray radiations or visible light of a different wavelength. Rare earths play a very important role in most of the phosphors. They are used in very small quantities dispersed in the matrix of the phosphor materials. They provide electrons that absorb the energy from the stimulus temporarily and later emit it in the form of light which has a characteristic colour. For example, red colour in the television picture comes from terbium doping. Sometimes they are used to just enhance the glow. Nd, Y, Tb and Eu are also used in various gadgets.

Rechargeable Batteries: This is one of the recent applications of RE materials. after the Nickel-Cadmium batteries came Nickel Metal Hydride (NiMH) rechargeable batteries. Electrodes in these batteries are supposed to absorb and release hydrogen ions, a job that rare earths do well. La, Ce, Pr and



Nd are used along with Nickel in the electrodes. These batteries are used in hybrid vehicles (which have both IC engines and electrical motors). Fully electrical vehicles are slowly going towards Li-ion batteries, which are yet not ready for heavy duty applications.

Nuclear Reactor Control: Gadolinium and dysprosium are important materials for the nuclear industry. They are strong absorbers of neutrons and hence used in emergency shutdown systems of the reactors. Nuclear reactors employ many safety features and mechanisms to control power, but they need some finite response time. If a shutdown is desired very quickly in an emergency situation, a solution of gadolinium nitrate $[Gd(NO_3)_3]$ is injected into the system. Very aptly this is called liquid poison. Dy can be used in Control Rods in solid form also.

Other Uses: From numerous other uses two need a mention here. Nd:YAG Laser is a popular type of Laser. The Yttrium argon Garnet Laser uses two of the RE family and is used in ophthalmic surgery to open the capsule around the eye lens. A new concept of magnetic refrigeration was first proposed in 1992. It uses the magnetic caloric effect observed in compounds like cerium magnesium nitrate which cools down when taken in and out of the magnetic field. The idea awaits being put in practice.

Politics and Economics

As more and more devices are invented which need rare earths for their functioning, their costs and availability are undergoing major fluctuations. When their only use was as catalysts, in 1970s and 80s, the United States was the main supplier for the world.

Incidentally, when China adopted the free market economy during the 1990s, the demand for RE was rising. Many Chinese companies entered the RE business as China had the largest known deposits. They increased their production so rapidly that their production was in larger proportion to their reserves as compared to other nations. This continued till 2010-11 when they realised the long-term strategic value of their deposits and at the same time became conscious of the environmental issues. They abruptly decreased the output and also the export quota. Prices in the international market went up almost ten times. For example, neodymium which sold at $45/kg went up to $450 and dysprosium from $300 to $3700 per kg in 2011.

Later a trade war erupted between the USA and China over the alleged spying charges on the Chinese telecom company Huawei. China is said to be using rare earths as a weapon because a shortage of these materials results in a slow-down in high tech products and thus affects the US economy, particularly the trade in modern technology items.

The USA imports REs worth 140 million dollars from China; but the restrictions affect both of them equally. A side story to this trade war is the varying estimates of Chinese resources. In 2009 the government news agency *Xinhua*, had quoted resources as 52 million tons, which was said to be 58% of the world reserve. Some years later *People's Daily* gave a figure of only 24%; whereas the USA thinks China has only 35% of the world stock.

Though Russia has the second largest reserves, they have not invested in separation technology and thus they export only aggregates. Unless the importing nation has the capacity to separate different rare earths, purchasing REs from Russia does not make sense. Due to the critical situation with regard to supplies, the world has turned its attention to recycling of the REs. This is a timely thought but its implementation will demand patience as the REs in most of the devices are thinly distributed.

As we come to the end of the story of rare earths, we understand that they are not as rare in *occurrence* as the name would suggest but rare in *availability* due to difficult separation. They are a tribute to the scientists who crafted the periodic table because they validate the logic behind the arrangement of the table. The rare earths are important also because they alone can gift us the gadgets of the modern life, more importantly the green technologies that reduce carbon dioxide emissions.

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