Rare Earths—the 21st century metals

Note that this is an <u>undergraduate</u> paper submitted as part of the requirements for completion of the GEOL 300 course at Vancouver Island University, BC, Canada. It may therefore contain errors, and should not be regarded or cited as an authoritative source. It does not contain any information derived from unpublished research. I hope nevertheless that some student somewhere will find it helpful as it represents a lot of work on my part. (Yes, I did pass the course with an A–).

<u>Errors and omissions</u>

It should have been noted in Figure 9, page 13, that the orbitals of electrons in the same subshell are always aligned so that their collective orbital is as spherically symmetrical as possible. The s-subshells always have perfect spherical symmetry, but the p-, d-, and f-subshells are only perfectly spherically symmetrical when half-filled or filled as is the case for europium and ytterbium (page 22).

<u>Date posted</u>:
November 30, 2013.

Rare earths:
the 21st-century metals
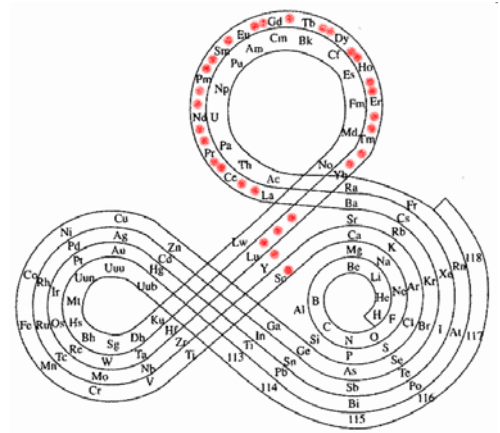
Nick Doe

Eudialyte: $Na_4(Ca,Ce)_2(Fe,Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$

Term Paper GEOL 300 (Instr. Casey Brant)
Vancouver Island University

April 2013

Rare earths—the 21st-century metals

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Term Paper submitted as part of course GEOL 300
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April 2013

*…I should hope that the purpose for which His Majesty commanded the expedition to
be undertaken will not be considered as having failed for want of zeal or perseverance,
though it should hereafter be found incomplete for want of judgement and ability.*

Captain George Vancouver, A Voyage of Discovery…, September 1795.

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Rare earths—the 21st-century metals

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ABSTRACT: Rare earth metals are playing an increasingly important role in new advanced technologies, but supplies of them are limited to only a few sources, notably in China. The need to learn more about their geochemistry and the petrology of their ores, and to develop economical and environmentally responsible extraction and re-cycling techniques is widely acknowledged. This paper reviews the history of the discovery of the rare earths; their growing economic and strategic importance; their atomic structure, and physical and chemical properties; the reasons for their so-called rarity, and the various types of ore-bodies that exist. Also reviewed are potential sources for the development of rare earth sources in Canada. These include the prospect at Hoidas Lake 50 kilometers north of Uranium City, Saskatchewan, and at Strange Lake on the Québec/Labrador border. Interest in rare earths in British Columbia as part of the NRCan/BCGS TGI-4 "specialty metal" program is also noted.

A profile of the rare earths

Metals in history

Metals have been prized and revered since ancient prehistoric times. Those that were known included copper; lead; mercury; tin; meteoric iron containing nickel; silver, which in Egypt was more costly than gold; and, of course, gold itself.

The development of metallurgical technologies in the Neolithic played an important role in the rise of later civilizations. Asia Minor, India, Europe, Korea, and China, all had periods in their prehistory known as Bronze Ages.[1] These endured from between five and six thousand years ago to a little under three thousand years ago. The Iron Ages, which followed the Bronze Ages, are similarly major archaeological periods, dating roughly from three thousand years ago to the Early Middle Ages in the first millennium of the Christian era.

By the end of the Middle Ages, alchemists knew how to produce antimony, arsenic, and zinc (as a metal),[2] but it was not until the Age of Enlightenment and the Industrial Revolution that the list of known metals began to rapidly expand.

Platinum had been discovered by the Spanish in Nueva España (Mexico) in the 1500s; metallic bismuth was also being used by artisans at about the same time, but, the mid- to late-18th century saw a rapid doubling of the number of known metals.

Those added to the list were cobalt in 1735; nickel in 1751; manganese in 1774; molybdenum in 1781; tellurium in 1782; tungsten in 1783; uranium and zirconium in 1789; titanium in 1791; yttrium in

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[1] Bronze is a alloy of copper and usually tin. Other alloys in use since early times are pewter (mainly tin) and brass (made from copper-zinc ores).

[2] Zinc, as a metal, was known to earlier smelters as a by-product, certainly in India and China, but was never highly valued. Strabo, a Greek geographer writing in Roman times refers to it as "mocksilver".

1794; and beryllium and chromium in 1797.

The Periodic Table of elements was pretty-much completed by the end of the 19th century, which saw the addition of over twenty new elements, most of which were rare earths. The only 20th-century hold-outs, apart from the synthetic transuranium elements,[3] were about five in number and included two more rare earth elements.[4]

What are rare earth elements?

According to the International Union of Pure and Applied Chemistry (IUPAC) there are seventeen rare earth elements (REEs), all of which are metals:

These are, with their atomic numbers and symbols:
scandium (21, Sc)[5] and
yttrium (39, Y) plus the fifteen lanthanides:
lanthanum (57, La)
cerium (58, Ce)
praseodymium (59, Pr)
neodymium (60, Nd)
promethium (61, Pm)
samarium (62, Sm)
europium (63, Eu)...........LREEs

gadolinium (64, Gd)   HREEs
terbium (65, Tb)
dysprosium (66, Dy)
holmium (67, Ho)
erbium (68, Er)
thulium (69, Tm)
ytterbium (70, Yb), and
lutetium (71, Lu).

Lanthanum to europium (45–63) are the "light" rare earths (LREEs) while gadolinium to lutetium (64–71) are the "heavy" rare earths (HREEs).[6]

The possible unfamiliarity of the names of the REEs may call for some help.[7] For a start, always pronounce the "y" in these names as if it were an "i"—as in "it".

Scandium (21) is Latin for Scandinavia, the peninsula where most REEs were discovered. Scandium was first found in Jølster, Norway (then part of Sweden).

Yttrium (39), Ytterbium (70), Erbium (68), and Terbium (65) are all names derived from that of Ytterby, a little town and quarry not far from Stockholm, Sweden, where minerals enriched in REEs were found in the late-18th century.

Lanthanum (57) is, appropriately enough, from the Greek for "hidden away".

Cerium (58) is derived from the name of the dwarf-planet Ceres, in turn from that of

Terbium Road near the Ytterby mine site.

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[3] The heaviest non-radioactive element has long been regarded as being bismuth (83), but most elements up to and including uranium (92) have long-lived isotopes. With the discovery that ^{209}Bi is radioactive, albeit with a half -life that far exceeds the age of the universe, the honour of being the heaviest non-radioactive element should now go to lead (82). Technetium (43), widely used in nuclear medicine, and promethium (61) are the only two elements that are both lighter than lead and without stable isotopes.

[4] This is a personal account, but while writing it, I did read and find interesting: Cramb (2013).

[5] The inclusion of scandium, whose compounds are intermediate between those of aluminium and yttrium, is traditional. Despite the IUCAP designation, scandium is commonly absent from lists of REEs.

[6]   Most of the LREEs were originally discovered in a mixed-oxide ore known at the time as "ceria"; and most of the HREEs were discovered in another mixed-oxide ore then known as "yttria".

[7] Much of the following information is from Weeks, ME. & Leicester, HM. 1968. *Discovery of the Elements*, Journal of Chemical Education, Easton, PA, USA.

a Roman goddess of agriculture and motherly love. Ceres was the first asteroid to be discovered, and its discovery in 1801, was just a year or two earlier than that of the element.

Praseodymium (59) and Neodymium (60) are Greek names meaning "green twin" (the colour of its oxide) and "new twin" respectively. The two were known for 50 years in chemistry books as "didymia" before their difficult separation. Pronounce "…dymium" as "…dimium".

Promethium (61) is radioactive; its salts glow in the dark. Its name is from Prometheus, a figure in Greek mythology who stole fire from the gods for human use.

Samarium (62) is from a mineral "samarskite" which in turn was from Colonel Samarski, a high ranking Russian mine official who granted access to ore bodies in the Urals to European mineralogists.

Europium (63) is from Europe. One of the transuranium elements is "americium".

Gadolinium (64) is after Johan Gadolin, a professor of chemistry in Finland who worked on the Ytterby ore. Most people say "gad…" as in "glad", not as in "gay, but talk to people from Gabriola about this.

Dysprosium (66) is from the Greek for "hard to obtain" (pronounced disprosium).

Holmium (67) is from the Latin name for Stockholm. "Holm" means islet.

Thulium (69) is from Thule (pronounced too-lee), not from the name of that car rack company, but from the son of Thor, an old name for Scandinavia.

Lutetium (71) is from the Lutetia, the name of the Roman town that is now Paris. It was discovered by Georges Urbain, an accomplished French chemist.[8] Pronounce it "loo-TEE-she-um".

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[8] Though the Austrian chemist Carl Auer von Welsbach discovered it independently and called it "neo-ytterbium" and later "cassiopeium". He also discovered ytterbium, named "aldebaranium".

REE minerals and properties

Many of the minerals containing REEs have perhaps equally unfamiliar names: allanite, parisite, bastnäsite, monazite, loparite, and dozens more; however, REEs are sometimes found in more than trace amounts in, for example, apatite (a phosphate), fluorspar (fluorite), zircon,[9] titanite (sphene), and perovskite.

All of the REEs are silvery-white metals—photographs of samples all look the same.[10] Many are moderately hard, but some are softer and several can be cut with a knife. Most tarnish in moist air. You are not likely to come across REEs as elements, but since they are heavy metals, if you did, they would resemble freshly-cut lead.

REEs are mostly traded as rare earth oxide powders (REOs). Many of these are white or whitish with a tinge of various colours—erbium oxide is slightly pink; neodymium oxide is bluish-grey—but some oxide powders are black or almost-black brown.

The majority of the REEs have a valency of three, and the most common oxides are X_2O_3 but there are also some very stable dioxides, XO_2.

REEs are marketed as metals and as simple compounds—chlorides, acetates, carbonates, etc.

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[9] Zircon is also well-known to geologists because it is used for radiometric dating of rocks, a method that depends on the presence of small amounts of uranium and thorium, which like the REEs are transition metals.

[10] Why? is a good question. Of all the metals, only copper, which untarnished is pink, and gold have obvious colour, but silver, europium, and ytterbium are actually the very palest of yellows.
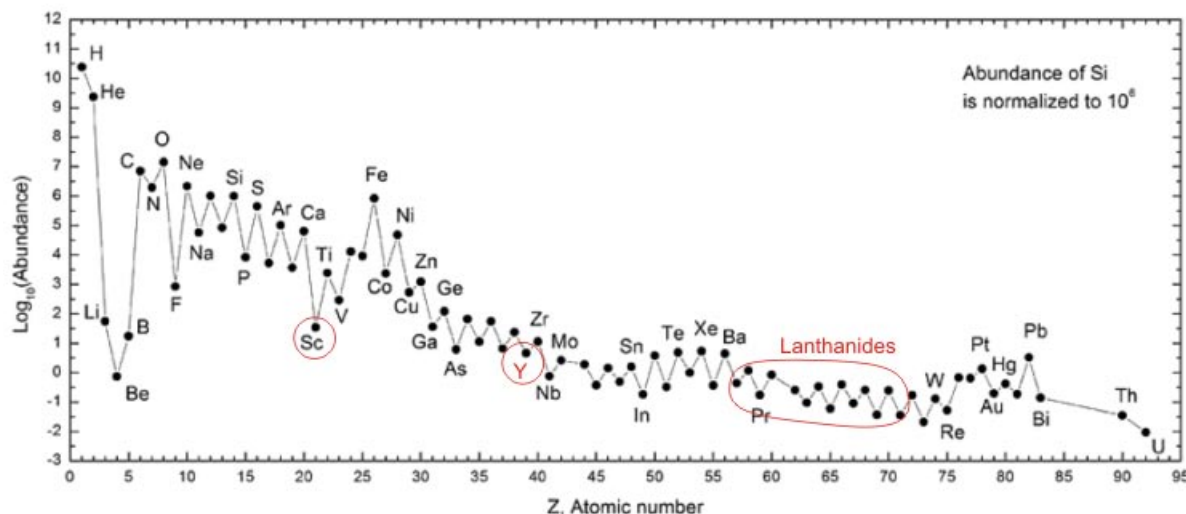
Figure1: Abundance of elements in the solar nebula. The REEs (red), along with scandium and all elements heavier than iron, were created by nucleosynthesis in supernova explosion(s) and were constituents of the gas and dust cloud that collapsed to form the solar system.

adapted from http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements

Applications

Until about four decades ago, the seventeen rare earth elements (REEs), "dwelt in obscurity" as the Biblical saying goes. Many people were only aware of them as existing in an add-on to the long-form of the Periodic Table of elements, often only identified by their symbols.

Like one of the more familiar groups of metals—chromium, cobalt, iron, manganese, etc.—the REEs form a transition series in the Periodic Table, and they have, in some ways, very similar—in some cases almost identical— physical and chemical properties, but in other ways, individual variations that make them of increasing interest in today's hi-tech industries.

As one might expect, innovative usage of these unusual metals in the defence, aerospace, nuclear, and electronic industries is high, but also noteworthy is their finding of applications in so-called "green" technologies. REEs are used in significant quantities in the manufacture of batteries in hybrid cars, catalytic converters in exhaust systems, large wind turbines, solar panels, and electric motors.[11] They also have potential uses as hydrogen storage containers, and for very efficient hydrofluorocarbon-free magnetocaloric refrigeration.

Apart from numerous industrial, medical, and optical applications, a few examples of products that incorporate REEs, perhaps unexpectedly, are euro bills that use an europium-based anti-counterfeiting phosphor; and cigarette-lighter flints from a gas station near you that use cerium and various other rare earths in small amounts.

Tent poles are made of a scandium-aluminum alloy to give them the required

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[11] Maybe stung by the criticism that the extraction of REEs is seldom done in an environmentally friendly manner, there are the beginnings of moves (2012) to develop "rare-earth free" motors and turbines, but it remains to be seen if this movement will develop any traction. There are also economic incentives of course to minimize REE usage.
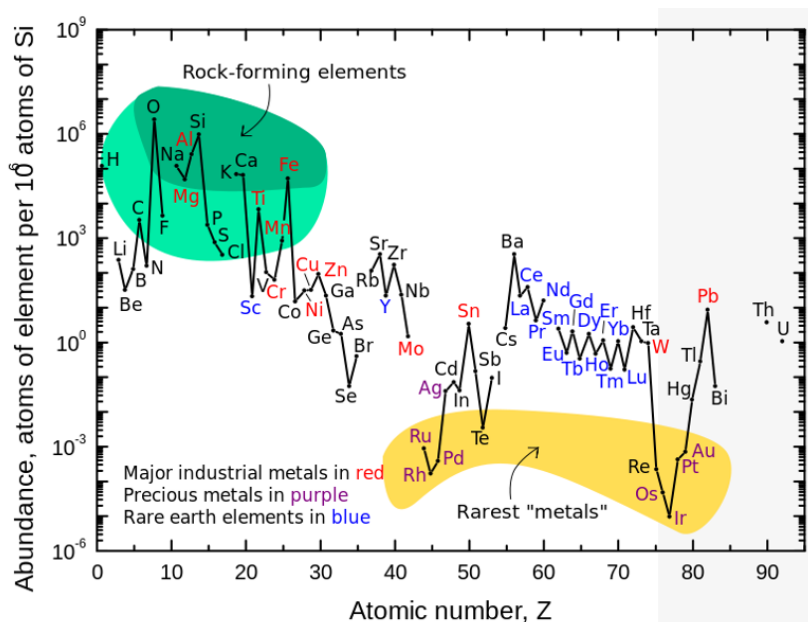
Figure 2: Abundance of elements in the earth's crust. REEs (blue) are no scarcer than more familiar industrial metals (red), their "rareness" is a consequence of the lack of natural processes to concentrate them into ores.

From US Geological Survey Fact Sheet 087-02

"springiness". And one of the reasons you may never have heard of samarium is that it is (or was) used in stealth technology to absorb laser light from the guidance system of popular brands of surface-to-air missiles (SAMs).

Some uses of REEs exploit their electrical and magnetic properties—hi-temperature superconductors, permanent magnets, miniature hard drives, sonar transducers— some their electro-optical properties— lasers, LED and LCD displays, fibre optic glass, colour corrected high-intensity lighting—and some the hardness of some of their compounds—ceramic colorants, nanoparticle polishing agents, walls of self-cleaning ovens, and synthetic gemstones.

One of the REEs, promethium, has no stable isotopes and is used in gauges to measure the thickness of metals and

plastics, and is a possible power source for satellites and space vehicles.

REEs, along with other trace elements and isotopes, are also used in a myriad of ways by petrologists as "fingerprinting" agents, and for radiometric dating.[12]

Why are REEs so rare?

One of the questions that inevitably gets asked about REEs, is why are they so rare? And the answer is that they are, in fact, not unusually rare. Some are more abundant than many familiar industrial metals, but the REEs have much less tendency to become concentrated in exploitable ore deposits. REEs are everywhere, and hence

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[12] (Winter 2010a). Lutetium[176], which decays to hafnium (Lu-Hf), and samarium[147], which decays to neodymium (Sm-Nd), both with half-lives exceeding the age of the earth, are used by geologists to radiometrically date the oldest-known rocks in the on-going competition for bragging rights between Australia and Canada.

from a prospecting perspective, almost nowhere. Even ash from my wood-burning fireplace on Gabriola Island, whose bedrock in my neighborhood is shale, contains, according to an assay, 0.34 parts per million (ppm) of dysprosium and 0.29 ppm of gadolonium—but there are no plans to develop mines there anytime soon.[13]

Figure 1 shows the estimated abundance (by number of atoms) in the solar nebula. Within the group of heavier elements, there is no evidence of REE depletion.[14]

A second figure, Figure 2, shows the abundance of elements in the earth's crust; and again, it's hard to make the case that they are unusually rare compared to other elements heavier than iron.[15]

Economics and politics of REEs

Economics

Because "high-grade" REE ores occur so rarely in nature, and when they do, their

Global rare earth oxide production trends
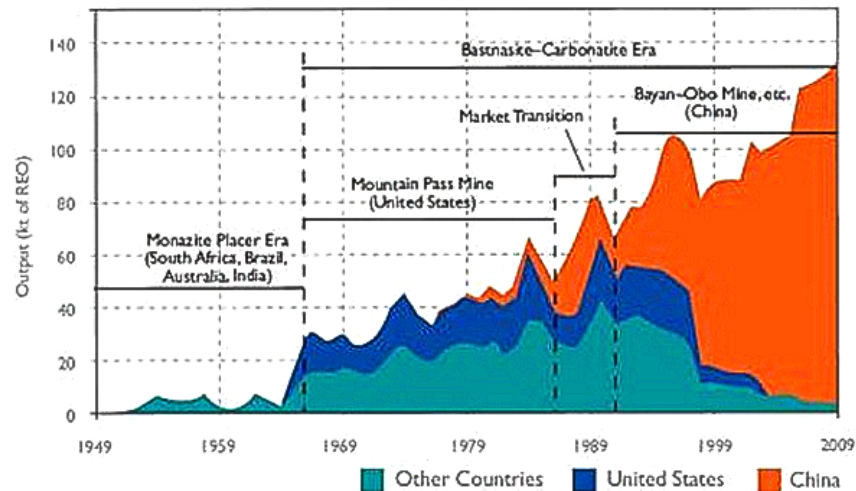
Figure 3: Global rare earth oxide production in kilotonnes from 1949 to 2009.

adapted from USGS Fact Sheet 087-02

concentration is so low,[16] production tends to be commercially viable in only a few large-scale operations, and often then only as a by-product in the production of other metals.

The United States once was largely self-sufficient in REE production, but in the past decade has become completely dependent upon imports from China, a trend established about ten years ago as shown in Figure 3. All of the other industrialized nations of the world have also come to rely almost exclusively on this single source.

In the absence of a "free market" with a multitude of suppliers, prices of REEs are currently very volatile. Some prices have quadrupled in the last three years and for

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[13] These are higher concentrations than that of cadmium. Yttrium and scandium are frequent trace elements in analyses of groundwater on the island.

[14] Studies of the distributions of the REEs in the earth's crust and mantle often use the distribution of REEs in chondrites (primitive stony meteorites) as a means of identifying geological processes that have, in one way or another, treated individual REEs differently.

[15] REEs are all *lithophile elements*, meaning they associate with the earth's crust rather than its core.

[16] To be considered viable for commercial development, REE ore content generally must be greater than approximately 1% by weight (USGS Open-File Report 2012–1016). This is roughly the same as for copper (0.4–0.8%) (USGS Professional Paper 820 1973).

some metals are now well over $100/kg.[17] Production volumes have dropt accordingly. China's exports were 43.9 kt in 2009, 39.8 kt in 2010, and 18.6 kt in 2011.

According to the China Daily, p.13, Aug.23, 2012, sales of REEs in 2011 went to:

Japan (56%); USA (14%)
France (10%); Hong Kong (6%)
Germany (3%); Italy (2%)
Netherlands (2%); South Korea (2%)
Vietnam (1%), and others (4%).

As is common in monopoly markets, accusations abound that the Chinese have been under-cutting rival suppliers, and then raising prices once the rivals have gone out of business. The Chinese defence is that low costs are the result of economies of scale, and low labour and infrastructure costs relative to the rest of the world; while, on the other hand, the subsequent higher prices are in the interests of conservation and sustainability and as a result of costs associated with environmental clean-up. All of which probably contains elements of truth.

Politics

Given the importance of a reliable supply of REEs to many hi tech industries, the supply economics has inevitably become politicised, with the World Trade Organization becoming involved in March 2012 at the behest of the USA, European Union, Japan, and 16 other countries including Canada (WTO Dispute DS431).

It should be noted however that it is not unusual for a minor metal commodity to be a monopoly market. The USA currently supplies 86% of the world

demand for beryllium, and 92% of the world's supply of niobium comes from just two mines in Brazil (USGS Scientific Investigations Report 2010–5220).

Quite apart from any difficulties, real or perceived, with relying on China for supplies of REEs, there is the political issue of so-called *conflict metals*. These are minerals mined in conditions of armed conflict and appalling human rights abuses, which at the time of writing, is the case in the Democratic Republic of the Congo. The Congo (formerly Zaire) is a source of illegally traded tin, tantalum, tungsten, gold, and other metals including REEs.

Currently, Canada does not mine REEs, but Canada and Australia have the potential to do so in the next few years. However, the extraction and processing of rare earths can cause considerable environmental damage, so not only marketing considerations are involved. This was the certainly the case in the decision to close the Mountain Pass rare earth mine in California in 2002.[18]

Recycling

While rare-earth companies are currently recycling rare earths from in-plant scrap, most notably in the manufacture of rare-earth magnets, recovery of rare earths from used products is not happening.[19] As always, cost effectiveness is the problem. Solving this will involve development of new separation technologies, establishment of collecting and stockpiling systems, and possibly "motivation through legislation".[20] ◊

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[17] REE prices vary with purity; in 2012 they were per kg: La $17; Ce $29; Pr $150; Nd $154; Sm $32; Dy $688; Eu $1393. Copper was $8/kg.

[18] It was re-opened by Molycorp in 2012.

[19] A UN Environmental Program report in 2011 put the amount being recycled at less than one percent.

[20] Tanaka et al. 2013.

Chemistry and physical properties of the REEs

The Periodic Table and atomic structure [21]

Figure 4 shows the familiar short-form of the Periodic Table.[22] The well-known benefits of this arrangement of the elements is that those with similar properties fall into columns—the alkali metals are in Group I on the left; the halogens are in Group VII; the noble gases that show very little or no chemical activity are all in Group VIII on the right; and so on.

Although the Bohr model of the atom is out-of-date, it still provides insight into why the elements can be categorized in this way. Bohr envisioned the structure of the atom as being analogous to the solar system with most of the atom's mass concentrated in a positively-charged nucleus surrounded by smaller and lighter negatively-charged electrons that orbited the nucleus at various distances.

The periodicity of the Periodic Table was explained by supposing that periods correspond to spherical shells which, beyond the Period 1, could contain up to eight electrons. Each shell was envisaged as being at an increasing distance from the nucleus, the shells closest to the nucleus being the ones with the least energy.

Chemical activity was seen in the Bohr model as a "desire" for atoms to have only full shells, and their willingness to achieve this by shedding outer electrons to form positive ions, as do the electropositive elements particularly in Groups I and II; to acquire electrons to complete the outer shell and form negative ions, as do the electronegative elements particularly in Group VII; and to share electrons in covalent bonds in the middle groups.

While the Bohr model is now known to be wrong, it was in remarkable agreement with many experimental facts and provided the first satisfactory explanation of the line spectra of hydrogen, but despite this success, it failed when applied to multielectron atoms. In particular, it provided no insightful description of the atomic structure of the transition elements, an understanding of which is essential to understanding their chemistry, particularly the chemistry of the REEs. For that we must turn attention to wave mechanics.

Quantum-mechanical models of the atom

In the quantum-mechanical model of particles, electrons and the quarks (which comprise protons) are to be viewed, not in the classical sense, as entities in space—like marbles in an otherwise empty shoebox—but as localized properties of space–like a tinge of colour if you will, even though space is, of course, colourless.

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[21] There are many sources for the information in this section. Because it was readily available, I mainly used: Cotton F.A. and Wilkinson, G., 1962. *Advanced inorganic chemistry—a comprehensive text*, Interscience Publishers. I also used Wikipedia Jan. 2013 for spot checks.

[22] The short-form table has eight columns and seven rows. The columns are known as groups, and the rows as periods. The first period contains only two elements, hydrogen and helium, but thereafter the periods each contain eight elements. The elements are entered into the table in the normal (Western) reading style, left to right, starting at the top and working down. The order is governed by the element's atomic weight, which corresponds to the number of protons in the nucleus.

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Period 1	Hydrogen 1							Helium 2
Period 2	Lithium 3	Beryllium 4	Boron 5	Carbon 6	Nitrogen 7	Oxygen 8	Fluorine 9	Neon 10
Period 3	Sodium 11	Magnesium 12	Aluminum 13	Silicon 14	Phosphorus 15	Sulphur 16	Chlorine 17	Argon 18
Period 4	Potassium 19	Calcium 20	Gallium 31	Germanium 32	Arsenic 33	Selenium 34	Bromine 35	Krypton 36
Period 5	Rubidium 37	Strontium 38	Indium 49	Tin 50	Antimony 51	Tellurium 52	Iodine 53	Xenon 54
Period 6	Cesium 55	Barium 56	Thallium 81	Lead 82	Bismuth 83	Polonium 84	Astatine 85	Radon 86
Period 7	Francium 87	Radium 88						

hydrogen	alkali metals	alkali earth metals	poor metals	metalloids	non-metals	noble gases

1st series 21-30	2nd series 39-48	3rd series 57-80	Actinides 89+	transition elements

Figure 4: The short-form of the Periodic Table of elements containing 44 elements. Numbers are the atomic number of the element (Z)—the integral number of protons in the nucleus and electrons around it.

1st transition series											
	19th century	18th century	19th century	18th century	18th century	antiquity	18th century	18th century	antiquity	13th century (India)	
Calcium 20	Scandium 21	Titanium 22	Vanadium 23	Chromium 24	Manganese 25	Iron 26	Cobalt 27	Nickel 28	Copper 29	Zinc 30	Gallium 31
Scandium is counted by IUPAC as one of the 17 rare earth elements, partly for historical reasons that not everyone now regards as significant											

Figure 5: The 1st transition series of 10 elements. Most were already known by the end of the 18th century.

2nd transition series											
	18th century	18th century	19th century	18th century	20th century	19th century	19th century	19th century	antiquity	19th century	
Strontium 38	Yttrium 39	Zirconium 40	Niobium 41	Molybdenum 42	Technetium 43	Ruthenium 44	Rhodium 45	Palladium 46	Silver 47	Cadmium 48	Indium 49
Yttrium is counted as one of the 17 rare earth elements because of its similarity to the lanthanides.											

Figure 6: The 2nd transition series of 10 elements. Many became known during the 19th century.

3rd transition series								
	19th century	19th century	19th century	19th century	20th century	19th century	19th century	19th century
Barium 56	Lanthanum 57	Cerium 58	Praseodymium 59	Neodymium 60	Promethium 61	Samarium 62	Europium 63	Gadolinium 64
	19th century	19th century	19th century	19th century	19th century	19th century	20th century	20th century
	Terbium 65	Dysprosium 66	Holmium 67	Erbium 68	Thulium 69	Ytterbium 70	Lutetium 71	Hafnium 72
	19th century	18th century	20th century	19th century	19th century	16th century (Mexico)	antiquity	antiquity
	Tantalum 73	Tungsten 74	Rhenium 75	Osmium 76	Iridium 77	Platinum 78	Gold 79	Mercury 80	Thallium 81
Lanthanides. These make up 15 of the 17 rare earth elements. The IUCAP also includes scandium (Z=21) and yttrium (Z=39).								

Figure 7: The large 3rd transition series of 24 elements. These perhaps unfamiliar names will, for sure, be better known in the 21st century.

Actinide elements (4th transition series)								
	19th century	19th century	20th century	18th century	20th century	20th century	20th century	20th century
Radium 88	Actinium 89	Thorium 90	Proactinium 91	Uranium 92	Neptunium 93	Plutonium 94	Americium 95	Curium 96

Figure 8: The actinides, an incomplete transition series trailing off due to the instability of the nuclei of transuranium elements.

The "particleness", to coin my own term, of any point in space, Ψ, reflects only the probability, ΨΨ*, that a classical particle will be seen at that location if an observation were to be made.[23]

Thus in the quantum-mechanical model, it is only possible to define a region of space with "particleness" around the nucleus in which an electron might be found, the Bohr radius of the hydrogen's electron being the distance from the nucleus where the "probability", meaning the radial probability density, is highest.[24]

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[23] Ψ is the wave function of the particle, commonly expressed when dealing with atoms in spherical co-ordinates as Ψ(r,θ,φ,t), where the value of Ψ is complex (two-dimensional). The separate dimensions of Ψ have no non-mathematical interpretation, but the value of the square of its magnitude ΨΨ*(r,θ,φ), which is a positive scalar, does. It is the time-independent square of the envelope of a stationary wave, and equals the probability of finding the particle at that particular location when an observation is made.

Of necessity, ∫ΨΨ*dr dθ dφ =1 when integrated over all allowed values of r, θ, φ, meaning that the particle exists with certainty somewhere in the space defined.

Negative values of Ψ (r,θ,φ,t) have no non-mathematical interpretation when only one particle is involved; but in multi-particle situations, they allow for cancellation in places where positive and negative values overlap. Regarded as waves, this amounts to destructive interference between the wave functions of the particles. Regarded as particles, it amounts to there being locations in space where a particle is never found, no matter how often one looks.

One other important consequence of negative values of Ψ is that a space can only contain one electron at a time even though their wave functions overlap (the Pauli exclusion principle). Mathematically this requirement is expressed as a requirement that $\int \Psi_1 \Psi_2\, dr\, d\theta\, d\varphi = 0$, where Ψ_1 and Ψ_2 are the wavefunctions of two electrons. This orthogonality requirement is only possible if Ψ may have negative values.

[24] Calculating the probability of observing an electron at various distances from the nucleus by

In the Bohr model, electron orbits were thought of as being circular, or in some failed attempts to extend the theory to atoms other than hydrogen, being elliptical. The geometry allowed by the quantum-mechanical interpretation is more complex, and more successful in explaining the chemical properties of elements.

One helpful visual aide to getting a feel for the complexity of this geometry is to consider the modes of vibration of a drum. A drum, with a membrane fixed at the rim, may vibrate in a simple pattern like this:
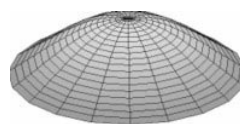
or, in more complicated ways, like these:

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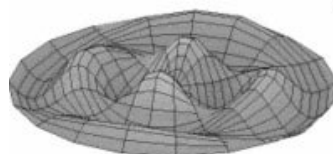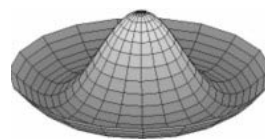
integrating the radial probability density with respect to dr, the thickness of a thin shell of radius r, is a standard physics student's task. The probability of observing an electron within the Bohr radius is 0.68 (68%). The probability of observing an electron within a radius 2.6 times the Bohr radius is 0.9 (90%).
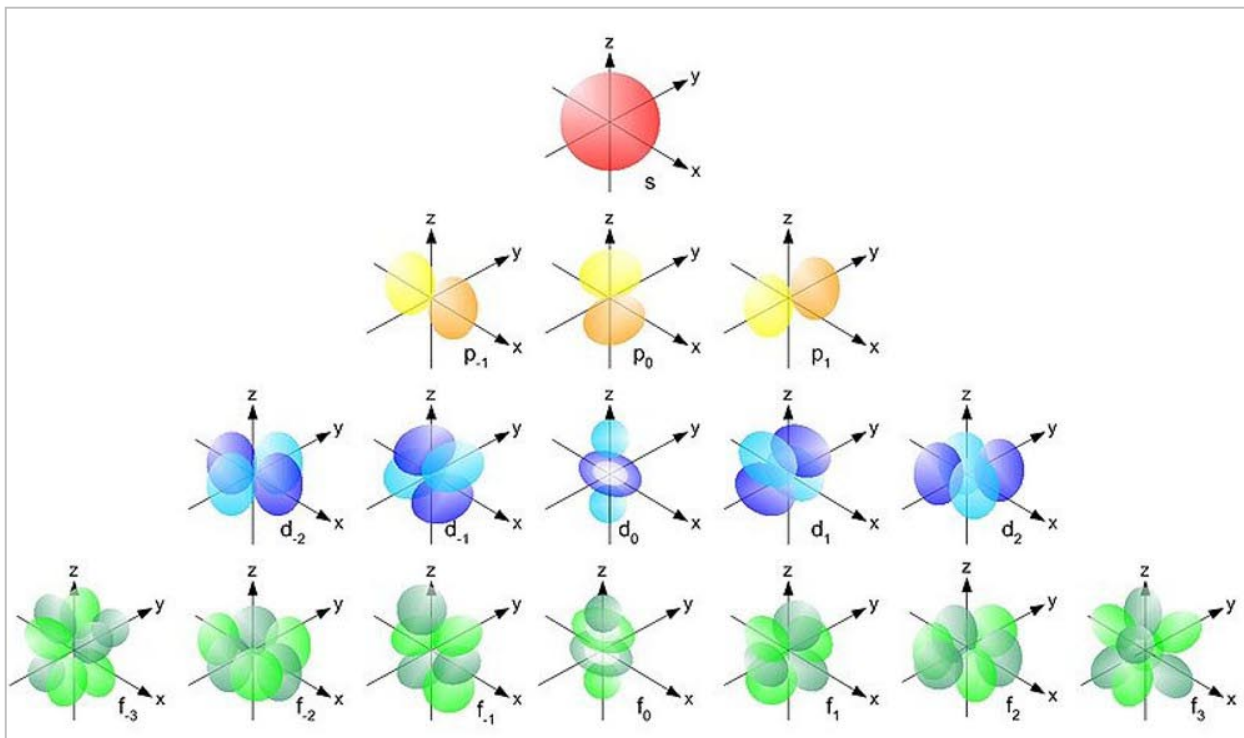
Figure 9: The geometry of the wave functions of electrons surrounding a nucleus. Just as a complex musical sound can be analyzed into a small number of modulated harmonics, so the "cloud" of electrons around a nucleus can be seen to be made up to 7 shells, each shell comprising up to four subshells (s,p,d,f), each in turn with 1, 3, 5, or 7 orbitals. Only the heaviest atoms have electrons described by all of these wave functions.

Wave functions are orthogonal functions (the different shades of colour for each function indicating + and –), meaning they are variables that can be added and subtracted from a subshell without effect on the other variables, just as you can precisely define the position of an object with only three numbers and can subsequently change one number without effect on the other two, or you can adjust the timbre of a musical note by modulating its harmonics without altering its pitch. Because each orbital may contain up to two electrons, the maximum number of electrons in the s-subshells is 2, in the p-subshells is 6, in the d-subshells is 10, and in the f-subshells is 14.

Unattributed at http://ts4.mm.bing.net/th?id=H.4587872086393707&pid=1.9

Complicated though these patterns are, they are obviously not random, and they can be characterized by a set of integers, in this case, two, that are related to the diameter of the drum, its circular symmetry, and the fact that the membrane is firmly attached to the rim.

The integers define, if you will, the order of the two-dimensional spatial and temporal harmonics.

In the quantum-mechanical world, the integers and half-integers that characterize the wave functions of electrons bound to the nucleus of an atom, are the quantum numbers of the electrons. These numbers, all of which are integers or half-integers, are the:

—principal number n, which is positive (but not zero);

—angular momentum number l, which is positive (including zero) up to $n–1$;

—magnetic number m, which is in the range $\pm l$ (including zero);

—spin number m_s, which can only be $\pm\frac{1}{2}$.[25]

Shells

For chemists, n corresponds to a *shell* in the Bohr model and indicates periods in the Periodic Table. All of the electrons in the same shell ($n, \dots$) have approximately the same energy, which increases as n increases.

Subshells

The quantum number l corresponds to a *subshell* within a shell. The energy of the electrons in a subshell increases slightly as l increases.

Electrons with quantum numbers ($n, 0, \dots, \pm\frac{1}{2}$) are said to be in the "s" (for sharp) subshell.

Electrons with quantum numbers ($n, 1, \dots, \pm\frac{1}{2}$) are said to be in the "p" (for principal) subshell.

Those with quantum numbers ($n, 2, \dots, \pm\frac{1}{2}$) are in the "d" (for diffuse) subshell

Those with quantum numbers ($n, 3, \dots, \pm\frac{1}{2}$) are said to be in the "f" (for fundamental) subshell.[26]

Orbitals

The quantum number m corresponds to *orbitals* within a subshell. Its importance lies in its relationship to the shape of the quantum-mechanical field and hence the geometry of molecular bonds.

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[25] Sometimes expressed as (clockwise or anticlockwise), (up or down), or ($\uparrow$ or $\downarrow$), the point being for present purposes that, call them what you will, there are only two options, just as we habitually use the symbols + and – for charge.

[26] The letters "s,p,d,f" are those used in early studies of the atomic spectral lines.

Spin

The fourth quantum number, m_s, is the spin, which affects the energy of the electron very little, but affects the magnetic properties of the atom.

Atomic structures of the elements

There can only be 2 electrons in the s-subshells: ($n, 0, 0, \pm\frac{1}{2}$).

There can only be 6 electrons in the p-subshells: ($n, 1, -1, \pm\frac{1}{2}$), ($n, 1, 0, \pm\frac{1}{2}$) and ($n, 1, 1, \pm\frac{1}{2}$).

There can only be 10 electrons in the d-subshells: ($n, 2, -2, \pm\frac{1}{2}$), ($n, 2, -1, \pm\frac{1}{2}$), ($n, 2, 0, \pm\frac{1}{2}$), ($n, 2, 1, \pm\frac{1}{2}$) and ($n, 2, 2, \pm\frac{1}{2}$).

There can only be 14 electrons in the f-subshells: ($n, 3, -3, \pm\frac{1}{2}$), ($n, 3, -2, \pm\frac{1}{2}$), ($n, 3, -1, \pm\frac{1}{2}$), ($n, 3, 0, \pm\frac{1}{2}$), ($n, 3, 1, \pm\frac{1}{2}$), ($n, 3, 2, \pm\frac{1}{2}$) and ($n, 3, 3, \pm\frac{1}{2}$).

This 2:6:10:14 pattern is seen in Figure 9 as $2 \times (1{:}3{:}5{:}7)$ combinations.

By convention, the arrangement of atoms in an element is written as, using aluminum as an example, [Ne] $3s^2 3p^1$ where [Ne] $\equiv$ [He] $2s^2 2p^6$ and [He] $\equiv 1s^2$

This signifies that the aluminum electron array has a neon core plus a higher-energy shell with a 3s-subshell containing 2 electrons and a 3p-subshell containing 1 electron. Neon, in turn, has a helium core plus a higher-energy shell with a 2s-subshell containing 2 electrons and a 2p-subshell containing 6 electrons. Helium, has no core array of electrons and its electron array is simply a 1s-subshell containing 2 electrons. In all, 13 electrons in shells of 3, 8, and 2, the outermost 3 in shell 3 being valency electrons.

These arrangements neatly explain the structure of the Periodic Table, a version of which with this detail is shown in short-form in Figure 11.

The valency (valence) of the elements in the short-form table is controlled by the number of electrons in the s- and p-subshells of the highest-energy shell. This number increases left to right, and the identity of the most energetic shell increases as you move down through the periods of the table.

Transition elements

The transition series of elements, which are depicted in the long-form of the Periodic Table, Figures 5, 6, 7, and 8, are those that lie in the Periodic Table between Groups II and III in Periods 4–7. There are three such series plus an incomplete transition series of unstable radioactive elements known as *actinides*. The REEs other than scandium and yttrium are in the third transition series.

If the electrons in the electron "cloud" around a nucleus did not interact with each other, the Periodic Table would not contain these so-called transition elements. In an atom with no electron interaction, the energy of the electrons in any subshell—s, p, d, or f—would be practically identical, and determined only by the principal quantum number, n, of the shell.

The effect of interaction between the electrons is to produce an energy spread within shells. The energy of electrons in s-subshells is less than the energy in p-subshells and so on in the order s<p<d< f. Transitions in the Periodic Table first occur when the lowest energy of the outer shell of the atom begins to overlap with the highest energy level of the next-to-last inner shell. This is illustrated in Figure 10.

The interaction between electrons that causes subshells to have different energy
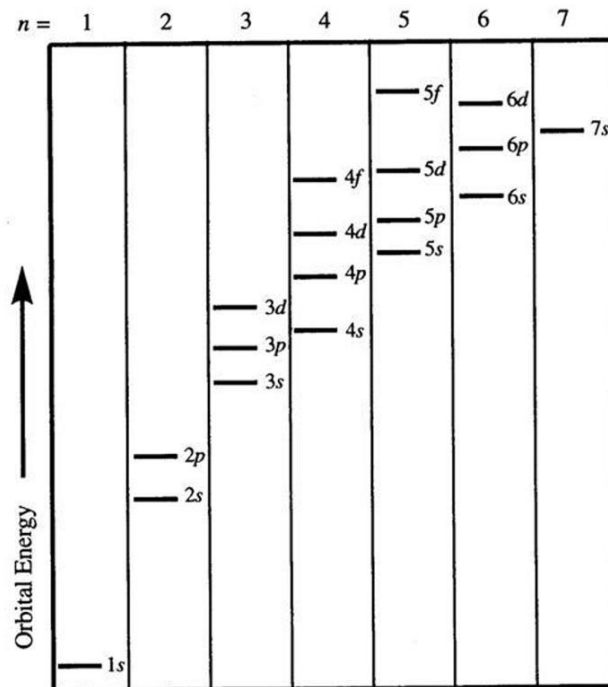
Figure 10: The energy levels (not to scale) of the subshells in shells 1–7. The spread within each shell is due to interactions between electrons. Note, for example, that the energy of electrons in the 4s-subshell is less than that of electrons in the 3d-subshell. Thus potassium (19) and calcium (20) are stable elements in Groups I and II even though their 3d-subshells are empty.

levels is complicated, but a feel for it can be gained by looking at Figure 9.

The energy level of the electrons in the higher-order shells is higher than it would otherwise be because they are shielded from the intense positive charge of the nucleus by the lower-order shells. But if you look at the geometry of the wave functions of the orbitals, you will see that electrons in the s- and d_0-orbitals have a geometry that actually includes the nucleus. There is therefore a very small, but non-zero, probability of a classical electron being found very close to, or even within the nucleus where it is not shielded from it.

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Period 1	H 1 $1s^1$							He 2 $1s^2$
Period 2	Li 3 [He] $2s^1$	Be 4 [He] $2s^2$	B 5 [He] $2s^22p^1$	C 6 [He] $2s^22p^2$	N 7 [He] $2s^22p^3$	O 8 [He] $2s^22p^4$	F 9 [He] $2s^22p^5$	Ne 10 [He] $2s^22p^6$
Period 3	Na 11 [Ne] $3s^1$	Mg 12 [Ne] $3s^2$	Al 13 [Ne] $3s^23p^1$	Si 14 [Ne] $3s^23p^2$	P 15 [Ne] $3s^23p^3$	S 16 [Ne] $3s^23p^4$	Cl 17 [Ne] $3s^23p^5$	Ar 18 [Ne] $3s^23p^6$
Period 4	K 19 [Ar] $3d^04s^1$	Ca 20 [Ar] $3d^04s^2$	Ga 31 [Ar] $3d^{10}4s^24p^1$	Ge 32 [Ar] $3d^{10}4s^24p^2$	As 33 [Ar] $3d^{10}4s^24p^3$	Se 34 [Ar] $d^{10}4s^24p^4$	Br 35 [Ar] $d^{10}4s^24p^5$	Kr 36 [Ar] $3d^{10}4s^24p^6$
Period 5	Rb 37 [Kr] $4d^05s^1$	Sr 38 [Kr] $4d^05s^2$	In 49 [Kr] $4d^{10}5s^25p^1$	Sn 50 [Kr] $4d^{10}5s^25p^2$	Sb 51 [Kr] $4d^{10}5s^25p^3$	Te 52 [Kr] $4d^{10}5s^25p^4$	I 53 [Kr] $4d^{10}5s^25p^5$	Xe 54 [Kr] $4d^{10}5s^25p^6$
Period 6	Cs 55 [Xe] $4f^05d^06s^1$	Ba 56 [Xe] $4f^05d^06s^2$	Tl 81 [Xe] $4f^{14}5d^{10}6s^26p^1$	Pb 82 [Xe] $4f^{14}5d^{10}6s^26p^2$	Bi 83 [Xe] $4f^{14}5d^{10}6s^26p^3$	Po 84 [Xe] $4f^{14}5d^{10}6s^26p^4$	At 85 [Xe] $4f^{14}5d^{10}6s^26p^5$	Rn 86 [Xe] $4f^{14}5d^{10}6s^26p^6$
Period 7	Fr 87 [Rn] $7s^1$	Ra 88 [Rn] $7s^2$						
common oxidation states	+I	+II	+III +IV	+IV +II to −IV	+III +V +IV −III	−II +VI +IV +II	−I +VII +V +III +1	0
oxides	X_2O	XO	X_2O_3	XO_2 XO XO_3^{2-} XO_4^{4-}	$X_2O_3.$ X_2O_5 XO_2 XO_3^- XO_4^{3-}	XO_3 XO_2 XO_3^{2-} XO_4^{2-}	X_2O_5 XO_3^- XO_4^-	

Figure 11: The electron configuration in the ground state of the short-form Periodic Table elements

	1st transition series											
	Ca 20 [Ar] $3d^04s^2$	Sc 21 [Ar] $3d^14s^2$	Ti 22 [Ar] $3d^24s^2$	V 23 [Ar] $3d^34s^2$	Cr 24 [Ar] $3d^54s^1$	Mn 25 [Ar] $3d^54s^2$	Fe 26 [Ar] $3d^64s^2$	Co 27 [Ar] $3d^74s^2$	Ni 28 [Ar] $3d^84s^2$	Cu 29 [Ar] $3d^{10}4s^1$	Zn 30 [Ar] $3d^{10}4s^2$	Ga 31 [Ar] $3d^{10}4s^24p^1$
common oxidation states	+II	+III	+IV	+V	+VI,+III	+VII,+IV, +II	+III,+II	+III,+II	+II	+II	+II	+III
oxides	XO	X_2O_3	XO_2, XO	X_2O_5 XO, XO_2, X_2O_3	X_2O_3 XO, XO_2 XO_3	XO_2 XO,X_2O_3, X_2O_7	X_2O_3 XO	X_2O_3 XO	XO	X_2O XO	XO	X_2O_3

Some chemists do not count zinc as a transition element, and copper's status is also occasionally questioned because its 3d-subshell is complete.

Figure 12: The electron configuration in the ground state of the 1st transition series. Note the break in the pattern at copper (29) which has an $[Ar]3d^{10}4s^1$ configuration instead of the expected $[Ar]3d^94s^2$. The energy gap between these two configurations is small, which is why copper absorbs blue light and appears pink to the human eye instead of absorbing only ultraviolet light and appearing white.

	2nd transition series											
	Sr 38 [Kr] $4d^05s^2$	Y 39 [Kr] $4d^15s^2$	Zr 40 [Kr] $4d^25s^2$	Nb 41 [Kr] $4d^45s^1$	Mo 42 [Kr] $4d^55s^1$	Tc 43 [Kr] $4d^55s^2$	Ru 44 [Kr] $4d^75s^1$	Rh 45 [Kr] $4d^85s^1$	Pd 46 [Kr] $4d^{10}5s^0$	Ag 47 [Kr] $4d^{10}5s^1$	Cd 48 [Kr] $4d^{10}5s^2$	In 49 [Kr] $4d^{10}5s^25p^1$
common oxidation states	+II	+III	+IV	+V	+VI +IV	+VII +IV	+IV +III	+III	+IV +II	+I	+II	+III
oxides	XO	X_2O_3	XO_2	X_2O_5 XO, XO_2	XO_2 XO_3	X_2O_7 X_2O_3 XO_2, XO_3	XO_2 XO_4	X_2O_3 XO_2	XO	X_2O	XO	X_2O_3

Some chemists do not count cadmium as a transition element.

Figure 13: The electron configuration in the ground state of the 2nd transition series. The difference between the energy of the $[Kr] 4d^{10}5s^1$ ground-state and $[Kr] 4d^95s^2$ states of silver is small and absorbs visible rather than ultraviolet light. If you look at white light reflected back and forth between parallel silver mirrors, it appears faintly yellow.

		3rd transition series							
	Ba 56 [Xe] $4f^05d^06s^2$	La 57 [Xe] $4f^05d^16s^2$	Ce 58 [Xe] $4f^15d^16s^2$	Pr 59 [Xe] $4f^35d^06s^2$	Nd 60 [Xe] $4f^45d^06s^2$	Pm 61 [Xe] $4f^55d^06s^2$	Sm 62 [Xe] $4f^65d^06s^2$	Eu 63 [Xe] $4f^75d^06s^2$	Gd 64 [Xe] $4f^75d^16s^2$
common oxidation states	+II	+III	+IV +III	+III	+III	+III	+III	+III +II	+III
oxides	XO	X_2O_3	XO_2 X_2O_3	XO_2 X_2O_3	XO_2 X_2O_3	XO_2 X_2O_3	XO_2 X_2O_3	X_2O_3	X_2O_3

		Tb 65 [Xe] $4f^95d^06s^2$	Dy 66 [Xe] $4f^{10}5d^06s^2$	Ho 67 [Xe] $4f^{11}5d^06s^2$	Er 68 [Xe] $4f^{12}5d^06s^2$	Tm 69 [Xe] $4f^{13}5d^06s^2$	Yb 70 [Xe] $4f^{14}5d^06s^2$	Lu 71 [Xe] $4f^{14}5d^16s^2$	Hf 72 [Xe] $4f^{14}5d^26s^2$
common oxidation states		+III	+III	+III	+III	+III	+III +II	+III	+IV
oxides		X_2O_3 XO_2 XO	XO_2 X_2O_3	XO_2 X_2O_3	X_2O_3	X_2O_3	X_2O_3	X_2O_3	XO_2

		Ta 73 [Xe] $4f^{14}5d^36s^2$	W 74 [Xe] $4f^{14}5d^46s^2$	Re 75 [Xe] $4f^{14}5d^56s^2$	Os 76 [Xe] $4f^{14}5d^66s^2$	Ir 77 [Xe] $4f^{14}5d^76s^2$	Pt 78 [Xe] $4f^{14}5d^96s^1$	Au 79 [Xe] $4f^{14}5d^{10}6s^1$	Hg 80 [Xe] $4f^{14}5d^{10}6s^2$	Tl 81 [Xe] $4f^{14}5d^{10}6s^26p^1$
common oxidation states		+V	+VI +IV	+VII +IV	+IV	+IV	+IV	+III	+II	+III +I
oxides		X_2O_5	XO_3 XO_2	X_2O_7 XO_2	XO_2 XO_4	XO_2	XO_2	X_2O_3	XO	X_2O X_2O_3

Lanthanum to europium (Z=57–63) are light rare earths (LREEs). Gadolinium to lutetium (Z=64–71) are heavy rare earths (HREEs)

Figure 14: The electron configuration in the ground state of the 3rd transition series. The valency of the REEs is +3, except for euopium (63), which hovers between +3 and +2. This is odd given that the outer subshell of the lanthanides contains only two electrons (s^2). The explanation for this appears to be that one of the 4f-subshell electrons has an orbital that keeps it well away from the nucleus allowing it to behave more like a 6s-subshell electron. The ground-state configuration of gold, $4f^{14}5d^{10}6s^1$ has only a slightly lower energy than $4f^{14}5d^96s^2$, which is why gold absorbs blue and red light and appears golden. Europium and ytterbium are like silver; they look white, but are actually an extremely pale yellow.

		Actinide elements (4th transition series)									
	Ra 88 [Rn] $5f^0 6d^0 7s^2$	Ac 89 [Rn] $5f^0 6d^1 7s^2$	Th 90 [Rn] $5f^0 6d^2 7s^2$	Pa 91 [Rn] $5f^2 6d^1 7s^2$	U 92 [Rn] $5f^3 6d^1 7s^2$	Np 93 [Rn] $5f^4 6d^1 7s^2$	Pu 94 [Rn] $5f^6 6d^0 7s^2$	Am 95 [Rn] $5f^7 6d^0 7s^2$	Cm 96 [Rn] $5f^7 6d^1 7s^2$	…	
oxides	XO	X_2O_3	XO_2	XO XO_2 X_2O_5	XO_2 XO_3 X_3O_8	X_3O_8 XO_2	XO_2	X_2O_3 XO_2	X_2O_3 XO_2		

Figure 15: The electron configuration in the ground state of the actinide transition series. Thorium (90) is sometimes found with REEs in the same ore body. Of etymological interest is "americum" (95) $5f^7 6d^0 7s^2$ named for its REE relative "europium" (63) $4f^7 5d^0 6s^2$.

Because the energy of an electron is related to its distance from the nucleus—the closer it is, the deeper it is in the nuclear potential well and the less energy it has—electrons in these particular orbitals have a lower than average energy, and this reduces the average energy in their respective subshells.

So, on one hand, shielding increases the energy level of f-subshell electrons, on the other hand, penetration of the core by the s-subshell electrons and the itinerant d-subshell orbital decreases the energy level of their subshell electrons.

The effect is felt particularly strongly in the s-subshells, so, for example, the energy of the 4s-subshell is reduced to below that of all the electrons in the 3d-subshell, and hence potassium has the configuration [Ar] $3d^0 4s^1$ (Figure 11), which is not the [Ar] $3d^1 4s^0$ configuration one might expect. The d-subshell only begins to fill with element [Ar] $3d^1 4s^2$ which is scandium, the first of the 1st transition series (Figure 12).

To give another example, cesium in Group I, Period 6 has the unexpected configuration [Xe] $4f^0 5d^0 6s^1$ (Figure 11), not [Xe] $4f^1 5d^0 6s^0$. The REE lanthanides in the 3rd transition series are left with the job of filling up the 4f-subshell from lanthanum itself [Xe] $4f^0 5d^1 6s^2$ to ytterbium [Xe] $4f^{14} 5d^0 6s^2$ (Figure 14). The remaining third series transition elements completes the 5d-subshell, and only then does short-form Periodic Table Group III service resume with thallium [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$.

As you look carefully at the electron configurations of the transition series (Figures 12–15), you might see why the status of some of the end-members of the series are occasionally questioned.

Iridium, for example, is [Xe] $4f^{14} 5d^7 6s^2$; yet platinum that follows it is [Xe] $4f^{14} 5d^9 6s^1$, not [Xe] $4f^{14} 5d^8 6s^2$.

Gold, which follows platinum, [Xe] $4f^{14} 5d^{10} 6s^1$, again not the [Xe] $4f^{14} 5d^9 6s^2$ one might anticipate. Only when we get to mercury, the last element in the 3rd transition series, [Xe] $4f^{14} 5d^{10} 6s^2$, is the "borrowed" 6s-subshell electron returned; a clear sign that not all d-subshell orbitals are created equal.

The colour of metals [27]

Why are the REE metals all a silvery white? They are, in this regard, not exceptional. All metals are in-a-sense coloured, they absorb certain wavelengths and reflect others; however, the colours absorbed by most metals are not perceptible by humans because the colours absorbed lie in the ultraviolet spectrum—which is why cerium has been proposed as a sun-screen ingredient. In white light, we say metals are colourless and shiny—but insects would strongly disagree.

There is a note on this, and the colour of copper, gold, silver, europium, and ytterbium in the captions of Figures 12, 13, and 14. [28]

Magnetic properties

REEs are paramagnetic at room temperature—they can be magnetized by an external field, but do not remain magnetic when the external field is removed. However, rare-earth magnets with higher than room temperature Curie temperatures can be made from REE-alloy

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[27] This section included at the request of Owen Peer, earth science technician, Vancouver Island University.

[28] Guerrero, A.H. et al. 1999. *Why gold and copper are colored but silver is not*, Journal of Chemical Education, 76 (2), p.200.

compounds. These are ferromagnetic and the strongest magnets known; large ones can easily injure human body parts and break bones when squeezed between them.

Rare-earth permanent magnets have many industrial applications, and magnets containing small amounts of neodymium are to be found in kid's science kits.

The magnetism is derived from the 4f-subshell which has seven orbitals, all of which can hold pairs of electrons with opposite spin, or single electrons with unmatched spin. The unpaired electrons in permanent magnets have their spin orientations aligned. The magnetism of iron arises in a similar way from electrons in the 3d-subshell; there are just fewer of them.

In magnetic prospecting, REE deposits can show as an abnormally high positive (paramagnetic, attractive) response or an abnormally low negative (diamagnetic, repulsive) response. Most other rare metal deposits are non-magnetic.

Some milling processes make use of REE ore magnetism to separate them from impurities.

Melting points

Information on the melting points of REE compounds is sparse, but the general trend can be gleaned from the well-established melting points of the metals, though the fluorides in particular have melting points ≈ 400°C higher than the metals. The metals themselves are refractory (the opposite of volatile).

The melting points for the HREEs are generally higher than for the LREEs as shown in Figure 16, europium and ytterbium, which are borderline
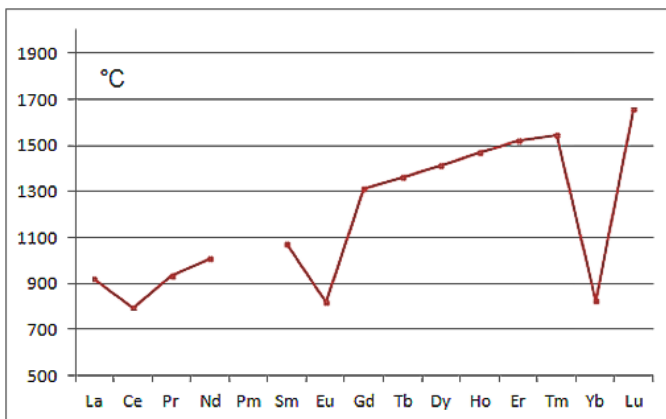

Figure 16: Melting point (°C) of REE metals at atmospheric pressure.

divalent/trivalent elements, bucking the trend. The higher melting points of the HREEs are a result of their higher atomic bonding strength. Atoms of the HREEs are smaller than those of the LREEs, so they have higher electric field strengths at their outer perimeters.

Superconductivity

Of the rare earth elements, only lanthanum is a superconductor as a pure metal, but high-temperature superconduction in REE alloys and compounds has been observed and is being actively researched. ◊

Geochemistry of the REEs

Geochemists have many overlapping interests with chemists, but of particular interest to geochemists is the valency, ionic size, and electronegativity of the REEs. These characteristics largely determine the compatibility or incompatibility of REEs in minerals, and ultimately in rocks.

Valency and oxidation states

Most REEs have a valency of +3 in their metallic state despite being on the borderline between the Group II (alkali earths) and Group III elements. The exception is europium, which has a valency of +2 in reducing environments, and +3 in oxidizing environments. Ytterbium and samarium may also show +2, but do so much less often.

An interesting theoretical calculation of valency energy that supports these empirical observations is shown in Figure 17.[29] If you equate valency with the number of electrons in the outer shell, the REEs will cause you trouble. All have an outer s-subshell containing just two electrons ($6s^2$). At least one of the electrons in the f-subshell must therefore be available as a valency electron. Europium and ytterbium are partial exceptions because their f-subshells are respectively exactly half full—one electron per orbital— and completely
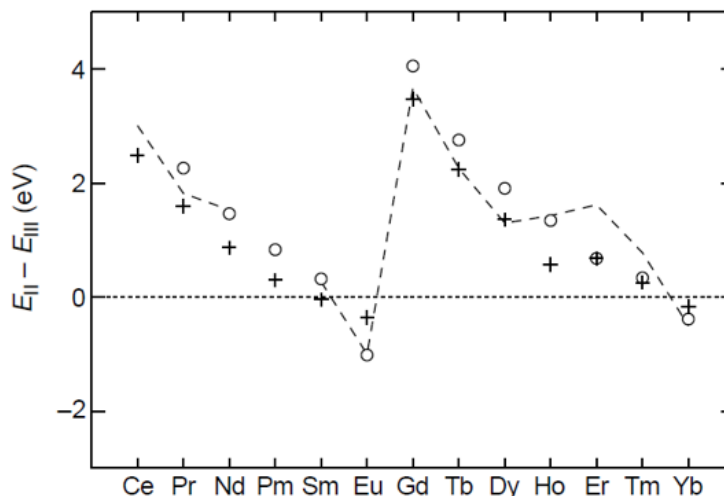

Figure 17: The Coulomb energy difference between valency energies 2 and 3 for the lanthanides. A positive value indicates the 3 valency is more thermodynamically stable. The open circles are calculations for metals; the crosses for sulphides.

Strange et al., 1999

full—two electrons per orbital—and this confers extra stability on their f-subshells.

All elements can exhibit oxidation states other than the lowest energy valency state of the element.[30][31] Thus although *RE*(III) is the characteristic state, *RE*(II) is known in many Eu^{2+} and some Yb^{2+} compounds;

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[29] Strange, P. et al. 1999. *Understanding the valency of rare earths from first-principles theory*, Nature, **399**, pp.756–8, June 24.

[30] This is particularly true of transition elements with only partially-filled inner and outer shells, and it's true of all elements when they are constituents of a molecule or crystal lattice. In these cases, it is the thermodynamical stability of the molecule or lattice as a whole that matters, not that of the individual atoms within it. Many molecules also exist only in a metastable state under particular environmental conditions.

[31] Just to be clear here, other definitions notwithstanding, I use "valency" to mean the most stable oxidation state (indicated with arabic numerals), and "oxidation state" to mean the number of electrons actually involved in a particular chemical bond. Oxidation states are conventionally indicated with Roman numerals.
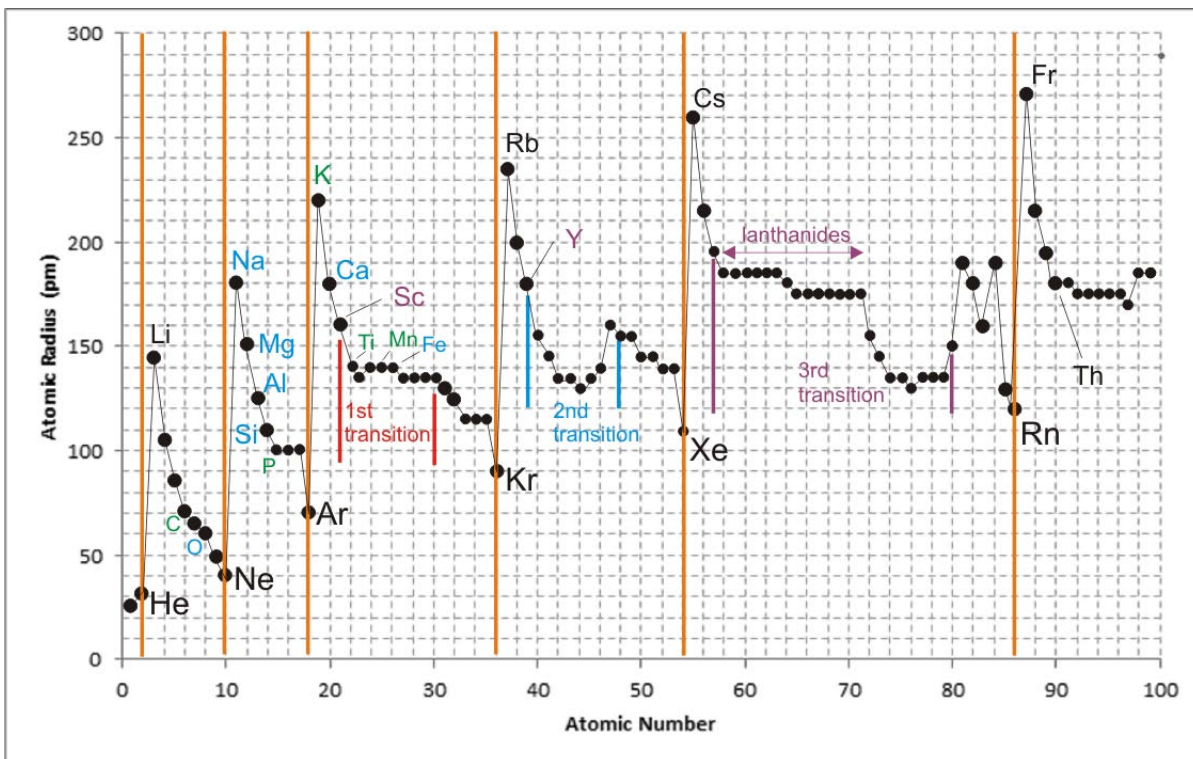
Figure 18: The atomic radii of the atoms plotted against atomic number. Atoms get slowly bigger moving period-to-period (delineated by the orange lines), within each period however, atoms get smaller as one moves from group-to-group. Major rock elements are blue, minor ones green.

Data from Wikipedia, Feb. 2013

RE(IV) is known, mainly in cerium compounds; and laboratories have reported RE(I) as Sc^+, Y^+, Gd^+, Tb^+. Oxidation states higher than RE(IV) do not exist.

Size

The size of an atom, whether reported as a radius or volume, is an ill-defined term that depends on whether the atom is neutral, ionized, or in a covalent bond. It also depends on what probability level is used for defining the "edge" of the electron wave functions (median and 90% are common choices).[32] One always needs to be careful when comparing sets of data, but the trends are the same. The size of

the REE ions is a major factor, along with charge, in determining in which mineral structures they may occur.

The size of atoms, shown in Figure 18, however it is measured, does not increase nearly as much as one might imagine as the atomic number goes up. A sodium atom, for example, is about the same size as a uranium atom.

Yttrium and the lanthanides have similar, fairly-large sizes, and their size, interestingly, is compatible with that of thorium and calcium, two element with valencies of 3±1 that REEs sometimes associate with in rocks.

Perhaps surprisingly, atoms of the heavy transuranium elements on the far right are not all bigger than much lighter atoms of

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[32] Physicists also sometimes use "atomic units" when dealing with atoms. One atomic unit (a.u.) is 52.9 pm (picometres).
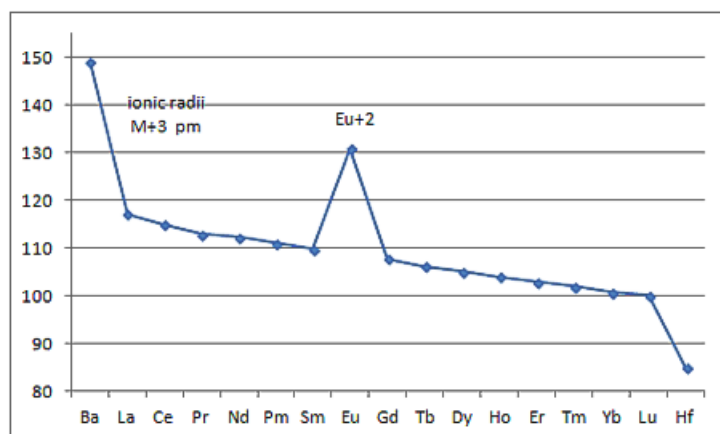
Figure 19: Ionic radii of barium–lanthanides–hafnium. For the M^{+3} ion except M^{+2} for europium and barium, and M^{+4} for hafnium. Yb^{2+} not shown.

Data from Wikipedia, Feb.15, 2013

elements like sodium and calcium. Their nuclei may be bigger, but their "clouds" of electrons are not. All of the 1st- and 2nd-transition series are smaller than the REEs.

Lanthanide contraction

Although not readily apparent in Figure 18, but shown in Figure 19, there is a steady drop in the size of the lanthanides as atomic number increases. This effect is responsible for subtle differences in the chemical and geochemical properties of individual REEs. These effects, small though they are, are of import because the REEs are almost identical in other ways. The size of REE cations also affects their distribution as exchangeable cations in zeolites and clays, and hence also in soils.

The so-called lanthanide contraction—it occurs in the other transition series too—is paradoxically, more easily understood as a lack of contraction. As the atomic number of an element is increased, so is the charge on the nucleus, and this draws the electrons closer to it. Within each period of the Periodic Table, it is to be expected therefore that the atoms get smaller as one moves from left to right. However, in the

3rd-transition series, adding one extra electron to the inner 4f-subshell in addition to adding one proton to the nucleus effectively reduces the net charge felt by the electrons in the outer 6s-subshell. They are partially *shielded* from the nuclear charge. The result is, the atom contracts, but not as much as it would otherwise.[33]

Electronegativity

Pauling electronegativity (χ) is a measure of the ability of atoms to attract electrons to itself. The electronegativity of the REEs is in the range 1.1–1.3, which is in the same ballpark as calcium and magnesium.[34]

The REEs are not amphoteric—meaning none form "lanthanates" or the elemental equivalent—although chemists have reported $[(RE,Al)F_6]^{3-}$ ions and they may probably occur naturally in deposits of the

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[33] I am not sure this explanation is entirely correct, but it is, for me, better than ones I sometimes see on the web. The only *partial* shielding is attributed in quantum-mechanical terms to the shape of the f-subshell orbitals. These allow the electrons in the 4f-subshell to distance themselves from the nucleus (see Figure 9), thereby losing their effectiveness as shields. "Contraction" also occurs in the other transition series.

[34] Pauling electronegativity has a low of 0.7 for francium (87), rising to a high of 3.98 for fluorine (9). Some electropositive elements (χ <2.5) are K 0.8; Na 0.9; Ca 1.0; Mg 1.3; Al 1.6; Zn 1.7; Fe 1.8; Si 1.9; and P 2.2. Some electronegative elements (χ >2.5) are S 2.6; C 2.6; Cl 3.2; and O 3.4.

Hydrogen's χ is 2.2. It could be argued that hydrogen, counted as a Group I element, would also fit in Group VII as a halogen—metal hydrogen halides (hydrides) exist—however, the electron affinity of hydrogen is low and hydrogen is far more often an electron donor than an electron receptor. The "neutral value" of χ, if there were such a thing, would therefore be around 2.5.

rare mineral cryolite (sodium hexafluoroaluminate).

Coordination numbers

The coordination number of REE atoms is usually in the range 7–9, which is not unusual for heavy metals, particularly less malleable ones with a body-centred cube structure.[35]

The relatively large size of the ions allows for a fairly high number of neighbours in crystal lattices, and correspondingly complicated chemical formulae for the minerals that contain them.

Aqueous solubility and weathering

REE oxides and hydroxides are only slightly soluble in water, and they behave much as do iron and manganese oxides in the natural environment. REEs will only stay in solution if:

—pH is low; the water is acidic because proton donors out-number proton acceptors; and/or

—Eh (redox potential) is low; the water is reducing because electron donors out-number electron acceptors.

A rise in the pH of groundwater at shallow depths is usually associated with the presence of carbonates.[36] Precipitation will also occur if the groundwater becomes oxygenated or there is a decrease in the dissolved organic carbon (DOC) content.

Many REE compounds dissolve readily and hence are rare to the point of non-existence in the geological world; an exception being the trifluorides, which are very insoluble. The solubility of the salts tends to decrease as the REE atomic number increases.[37] This is because the ionic radii become smaller (lanthanide contraction) and hence the field strengths of the ionic bonds (Z/r) in the solid become stronger. Less solubility leads to less basicity (they become more neutral).[38]

These differences enabled the early chemists to differentiate the REEs using repetitive fractional crystallization and fractional precipitation, techniques that mimic, in principle if not in detail, some of those that occur in nature.

Notwithstanding the above comments, the REEs are the least mobile elements during most metamorphic and weathering processes. ◊

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[35] In the crystallographic (not chemical) sense, coordination is the number of adjacent atoms in crystal lattices. The coordination number of iron, tungsten, vanadium, chromimum, etc is also 8 while that of gold, copper, silver is 12 (hexagonal and cubic close packed). Calcium's is 6–8; magnesium and potassium's are usually about 6; and sodium's is about 5.

[36] A rise in pH above ≈5 leads to cation exchange on rock surfaces ($3XNa+RE^{3+}\rightarrow X_3RE+3Na^+$). Tertre E. et al. 2007. *Rare Earth Element sorption by basaltic rock*, Geochimica and Cosmochimica Acta 72, pp.1043–1056.

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[37] In Cobar, Australia, leaching in the upper part of the regolith and enrichment in the lower zone close to the weathering front has been found to be significantly greater for LREEs than for HREEs. McQueen 2006 cited in Scott, KM. and Pain, CF. 2008. *Regolith Science*, Springer, Fig.6.20. However, while river water is typically enriched in LREEs relative to HREEs, this is far from being always the case in groundwater where pH and redox potentials are the controlling factors.

[38] La(OH)$_3$ solution has a pH of 8.7 at 20°C; and Gd(OH)$_3$ a pH of 7.9. Meloche, C.C. and Vrátný, F. 1959. *Solubility product relations in the rare earth hydrous hydroxides*, Analytica Chimica Acta, **20**: pp.415–418.

Mineralogy of the REEs

REE minerals

None of the REEs occurs in nature as a metal; they all tarnish readily in damp air and react slowly with cold water.

In general, minor elements like the REEs either substitute for more common elements in minerals, or they form rare minerals of their own. REEs however make poor substitutes, for although their +3 valency would seem to qualify them for aluminum stand-ins, their ions are 50–75% larger than aluminum ions. The only plagioclase that contains an REE is europium feldspar, in which europium (Eu^{2+}) substitutes for calcium, not for aluminum. Calcite in foraminifera shells also shows a positive europium anomaly.[39]

The REEs minerals are (surprise!) rare, and it is very common for REEs to substitute freely for each other in the minerals in which they do occur.

In the following section underlined minerals contain more than 50% by weight of REOs. (Castor, 2006).

Scandium mineralogy

Economic scandium ore bodies are not common and world production is concentrated in only a few mines. The main mineral is thortveitite $(Sc,Y)_2Si_2O_7$, an epidote-group with a double tetrahedra structure $[SO_3\text{-}O\text{-}SO_3]$ written $[Si_2O_7]^{6-}$.

Lanthanide and yttrium mineralogy [40]

Silicates

The lanthanide and yttrium silicates are nearly all orthosilicates (simple silicates without chained or framed tetrahedra), although the –4 charge on the SiO_4^{4-} ion calls for some ingenuity on the part of nature to match the valency of +3 of the REEs. Required are ions with negative charges that are multiples of three.[41]

Some lanthanide minerals make use of hydroxyl ions to accomplish this forming $[SiO_3.(OH)]^{3-}$ or $[(SiO_4)_2.(OH)]^{9-}$ ions, as in cerite.[42] $[Si_3O_{10}(OH)]^{9-}$ appears in thalenite.[43] REEs frequently mix common elements and hydroxyl ions to achieve charge-balance as in the allanites,[44] $M^{+5}[XY_2.O.SiO_4.Si_2O_7(OH)]^{-5}$. Substitute REEs in zircon may also contain hydroxyl ions, or use phosphorus to maintain charge neutrality.[45]

A few lanthanide silicate minerals contain both tetrahedra SiO_4^{4-} and octahedra SiO_6^{8-} to give an average SiO_5^{6-} as does the garnet-group. These use other metals to reduce the charges, as in $(BSiO_5)^{3-}$ in stillwellite,[46] $(TiSiO_5)^{3-}$ in titanite,[47] and

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[39] Yasutaka Terakado et al. 2010. Calcium ions are roughly the same size as LREE ions.

[40] Footnotes in this section are from Wikipedia, Jan 2013. Online sources provide much more mineralogical data than is given in this overview.

[41] Linked tetrahedra pairs, $Si_2O_7^{6-}$ occur. Eudialyte, whose formulaic representation includes the cyclosilicate $[Si_3O_9]^{6-}$ and $[Si_9O_{27}]^{18-}$ may also represent a lonely exception to the no-link rule.

[42] Cerite is a complex silicate. There are Ce- and La- rich species. Their common formula is: $(Ce,La,Ca)_9(Mg,Fe^{+3})(SiO_4)_6(SiO_3OH)(OH)_3$.

[43] Thalenite-Y is $Y_3Si_3O_{10}(OH)$.

[44] Allanites (orthites) belong to the epidote group. There are three: allanite-Ce, -Y, and -La. They often contain U, Th, and other elements. M^{+5}, on average, is $X^{2+}Y^{3+}$ where X is a large divalent cation (Ca,Sr,Mn) and Y is a trivalent cation (Al,Fe^{3+}). Trivalent REEs adapt this configuration to $X^{3+}Y^{2+}$ as in $RE^{3+}Fe^{2+}$.

[45] Zircon is $ZrSiO_4$. Some varities may contain $[RE(OH)]_2.SiO_4$ or a $ZrPO_4^+ : ZrREO_4^-$ mix.

[46] Stillwellite is $(Ce,La,Ca)BSiO_5$.

$(FeBe_2Si_2O_{10})^{6-}$ in gadolinite.[48] Mosandrite has a memory-challenging formula that includes some disilicate (soro) Si_2O_7.

There is more on the structure of silicates and their general unfriendliness to REEs later in this segment.

Halides

Although halides of the lanthanides are well known to chemists, only the fluorides are insoluble in water, so these are by far the most common, as in fluorcerite, $(Ce,La)F_3$. Some fluorite (CaF_2) deposits are rich in REEs. Fluoride ions F^- often stand-in for OH^- ions in REE minerals.

REE trifluorides have high melting points up to 1430°C.

Carbonates

Carbonatite rocks are formed by the interaction of carbonates and undersaturated mafics in the mantle. These mineral contain $[(CO_3)F]^{3-}$, notably as in one of the more common REE minerals, bastnäsite.[49] Parisite,[50] another carbonatite REE mineral, contains $[Ca(CO_3)_3F_2]^{6-}$. Some economic REE deposits contain minerals with $[(CO_3)_2.OH]^{5-}$ or $[(CO_3)_2.F]^{5-}$. In these, the REE combines with a divalent ion to make up the required +5 charge.[51] Kainosite contains $[(SiO_3)_4CO_3]^{-10}$ and

does the same with two divalent ions, usually, $Ca_2RE_2^{10+}$.

There is more on the structure of REE-carbonates later in this segment.

Phosphates, vandanates, titanates, etc.

Britholite contains both SiO_4^{4-} and PO_4^{-3} ions. Non-silicate REE minerals include the phosphates PO_4^{3-}, known as monazites,[52] xenotime,[53] and and fluorencite.[54] Apatite $Ca_5(PO_4)_3(F,Cl,OH)$ often contains REEs. There is also a rare vandanate VO_4^{3-}, as in wakefieldite.[55]

Aeschynite,[56] a curious mineral of varying compositions, contains tantalates, titanates, and niobates, though some of these are just mixed oxides. $Ce^{3+}Fe^{3+}$ is a rare substitute for $Ca^{2+}Ti^{4+}$ in petrovskite $(CaTiO_3)$. REE traces also substitute for Fe in ilmenite $(FeTiO_3)$.

Sulphates and Sulphides

The REE sulphates are very soluble. You sometimes come across them in hydrological studies as they are used as both natural and artificial tracers. REE sulphides however are not stable in water.

Oxides (REOs)

The REEs were originally known from their occurrence in oxide mixtures, "earth"

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[47] Titanite (sphene) is $CaTiSiO_5$ but often contains Ce and Y. Ca may be partly replaced by Th.

[48] Gadolinite (ytterbite) is another mineral with mixed composition $(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10..}$

[49] Bastnäsite comes in three flavours: bastnäsite-Ce, -La, and -Y. These are respectively $(Ce,La)CO_3F$; $(La,Ce)CO_3F$; and $(Y,Ce)CO_3F$.

[50] Parisite is $Ca(Ce,La)_2(CO_3)_3F_2$. Related cebaite is $Ba_3Ce_2(CO_3)_5F_2$, containing $[(CO_3)_5F_2]^{12-}$.

[51] Ancylite $SrRE(CO_3)_2OH$, huanghoite $BaRE(CO_3)_2F$, synchisite $CaRE(CO_3)_2F$.

[52] There are four monazite phosphates:
 Monazite-Ce $(Ce,La,Pr,Nd,Th,Y)PO_4$
 Monazite-La $(La,Ce,Nd,Pr)PO_4$
 Monazite-Nd $(Nd,La,Ce,Pr)PO_4$
 Monazite-Sm $(Sm,Gd,Ce,Th)PO_4$.
They usually contain traces of SiO_2, U, and Th.

[53] Xenotime is YPO_4 but the Y may be replaced in secondary amounts by Dy, Er, Tb, Yb, Th, or U. It is called churchite in its hydrated form.

[54] Fluorencite is $(La,Ce,)Al_3(PO_4)_2(OH)_6$.

[55] Wakefieldite is $(La,Ce,Nd,Y)VO_4$.

[56] Aeschynite occurs as:
Aeschynite-Ce $(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$;
Aeschynite-Y $(Y,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$; and
Aeschynite-Nd $(Nd,Ce,Ca,Th)(Ti,Nb)_2(O,OH)_6$.

being the old-fashioned name for an "oxide". REOs occur in half a dozen minerals. In natural conditions they are dioxides, which are more stable in damp air than the sesquioxides (RE_2O_3) despite

Figure 20: Clockwise from top centre: oxides of praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium.

US Department of Agriculture

	Pl.	Am.	Bt.	Kfs	Mag.	Ilm.
La	0.30	0.36	0.23	0.13	0.66	
Ce	0.22	0.68		0.06		
Nd	0.19	1.6	0.34	0.04		
Sm	0.12	2.3	0.39	0.02	1.2	6.9
Eu	2	3.2	0.5	1	0.91	2.5
Gd			0.35	0.01		
Tb	0.14	2.4		0.02		6.5
Dy			0.2	0.97		4.9
Er			0.17	0.16		
Yb	0.1	1.8	0.17	0.01	0.44	
Lu	0.1	1.8	0.21	0.01	0.3	3.6
avg.	0.4	1.8	0.3	0.2	0.7	4.9

Figure 21: Partition coefficients of the REEs (ratio of solid to liquid phase at equilibrium) of common minerals in rhyolite. The higher the number, the more likely it is the element will enter the mineral crystals (plagioclase, amphibole, biotite, K-feldspar, magnetite, and ilmenite). Ilmenite ($FeTiO_3$) and rutile (TiO_2) are trace minerals in Nanaimo Group sandstones and shales.

Compiled by the author from databases at http://earthref.org
Feb. 2013

the REEs being mostly trivalent.[57]

In clastic sediments, REOs are commonly adsorbed by ferromanganese particulates and weathering rinds,[58] and some iron ore deposits are exceptionally rich in REEs.

The association of REEs with iron and manganese in ores is syngenetic—the oxides precipitate from fluids at the same time for the same environmental reasons—and is likely related to the ability of Fe and Mn oxides and oxyhydroxides to act as oxidants—as in thermite—creating scarcely soluble REE complexes.[59]

REEs as trace elements

REE atoms that substitute for others in common rocks are not of economic

samarskite is $(RE,U,Fe)_3(Nb,Ta,Ti)_5O_{16}$; yttrotantalalite is $(Y,U,Fe)(Ta,Nb)O_4$, cerianite is $(Ce,Th)O_2$, and cheralite is $(RE,Ca,Th)(P,Si)O_4$.

[58] de Baar et al. 1985. The degree of association of REEs with Fe-Mn oxides can show large differences between the LREEs and HREEs. Cerium is particularly attracted to manganese nodules in the ocean (Taylor & McLennan 1988).

[59] Koeppenkastrop, D. & De Carlo, DH. 1993. *Uptake of rare earth elements from solution by metal oxides*, Environmental Science & Technology, 27, pp.1796–1802.

[57] Itinerant *f*-subshell electrons are to blame; see Leon Petit et al. 2007. Anatase, a form of rutile, is TiO_2; brannerite is $(U,Ca,RE)(Ti,Fe)_2O_6$; euxenite is $(RE,Ca,U,Th)(Nb,Ta,Ti)_2O_6$; fergusonite is $RE(Nb,Ti)O_4$; loparite is $(RE,Na,Ca)(Ti,Nb)O_3$;
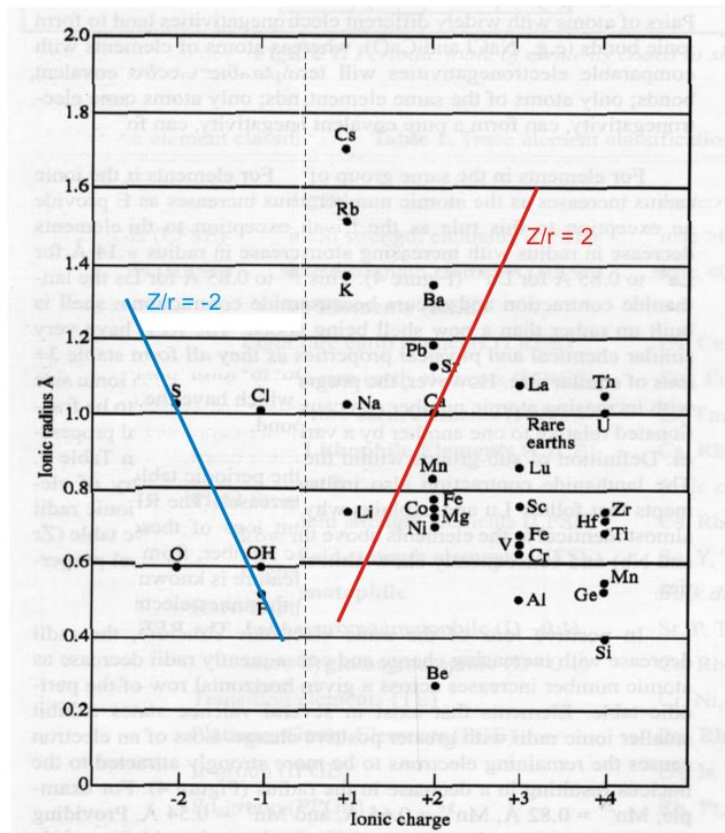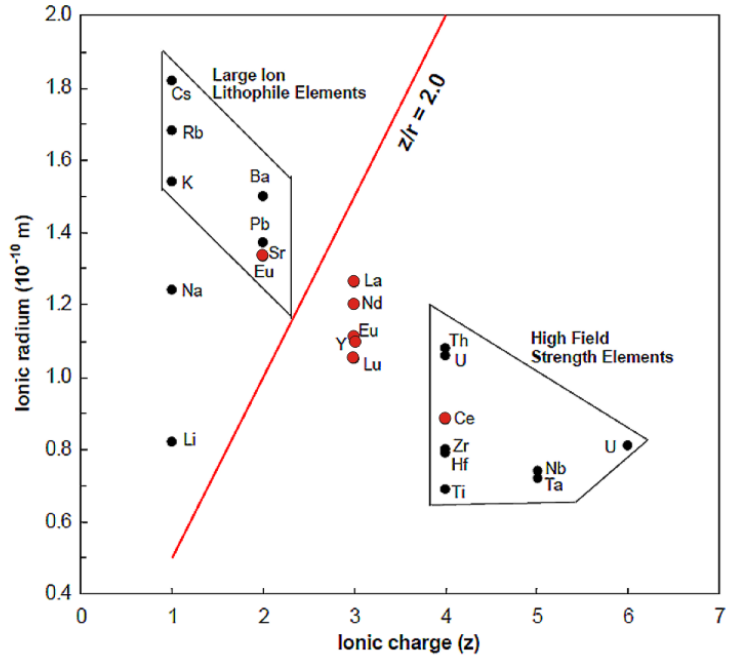
interest because of their very low concentrations, but, like all trace elements, they are often of great scientific interest. For those living in a felsic environment (BC Coast Mountain intrusives or Nanaimo Group sandstones), it is interesting to note from Figure 21 that it is probably hornblende that contains most traces of REEs. The table shows the partition coefficients of rare earths in rhyolite, the volcanic equivalent of granodiorite. The europium (Eu) anomaly in plagioclase (pl) is due to its extra-ordinary divalent nature and is common.

Ionic charge to ionic radius ratio

The ratio of the charge on an ion (Z) to its radius (r) is commonly taken to be a measure of the compatibility of the ion. Those elements whose ions have a large Z/r ratio are called high field-strength elements (HFSE); and those elements whose ions have a low Z/r ratio are low field-strength elements (LFSE), but are more usually called large-ion lithophile elements (LILE).[60]

Ions with significantly different Z/r ratios tend not to replace each other. They are said to be

Figures 22. Adapted by the author from various sources.

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[60] Lithophile is a preference for silicate over sulphide (chalcophile) and metal (siderophile). All REEs are lithophiles, but many transition elements are not.

incompatible. However, the reverse is not necessarily true. Ions with large charges and large radii may have the same ratio as those with small charges and small radii,

but it does not necessarily follow that they are compatible.

This point is well made in the two diagrams above. Although chemists classify the REEs as HFSEs—they're to the right of the dividing line—geochemists more often think of them as being a subset all of their own (Jenner 1996).

Notice the REEs (except Eu^{2+}) could make themselves more compatible with LILEs by reducing their charge (moving left) and slightly increasing their size (moving up). This is exactly what they do in the minerals containing $[RE^{+3}.(F^-,OH^-)_n]^{+3-n}$, and $[RE^{+3}_p.(CO_3^{2-})_q F^-_r]^{+3p-2q-r}$ ions, fluorine, oxygen, and carbon being among the smallest elements. Notice also that chlorine is too big to stand-in for fluorine, as are the other halogens.

Associations with other elements

REEs are almost always present in rock samples, even if in extremely small concentrations detectable only in mass spectrometers. At these low concentrations, well-defined minerals might not exist. An example would be REO_4^{5-} as a rare substitution for silicon in an SiO_4^{4-} ion. This requires the presence of, say, phosphorus as PO_4^{3-} to restore electrostatic neutrality.[61]

There is a variety of reasons why REEs might associate or disassociate themselves with other elements, some by parallel, but independent and not necessarily synchronous evolution, and others by paragenesis of varying degrees.[62]

Absence in common silicate minerals

All the most abundant minerals on the earth's surface—quartz, feldspars, pyroxenes, amphiboles, micas, and clay minerals—are based on the $[SiO_4]^{4-}$ ion, which structurally, as we know, is a tetrahedron. However, unlike rectangular, triangular, and hexagonal prisms, and some higher-order polyhedra, you can't fill (honeycomb) a 3-dimensional space—or even a "thick" sheet of it— without gaps (interstices) using tetrahedra alone. You can however completely fill a space with a mix of tetrahedra and octahedral, as is done in pyroxenes, amphiboles, and clay minerals.

For the severely geometrically-challenged, like myself, most diagrams of the structure of silicate minerals are meaningless once you get much beyond the chain-ring-sheet-framework possibilities of linking tetrahedra.[63] Suffice it to say, in varying degrees, the size and charge on the cations needed to balance the charge on the tetrahedra is restricted by the geometry, and in practically all cases, REEs just don't fit.

In orthopyroxenes, $XYSiO_3$, the interstitial sites demand smallish cations X and Y of equal radius and charge—Mg^{2+} 86 pm (picometres), Fe^{2+} 75 pm.

In clinopyroxenes, $XYZSiO_3,X(AlSi)O_3$, the different structure allows unequal sizes and charges—$(X^{+2}Y^{2+}T^{-4})$, $(X^{+1}Y^{3+}T^{-4})$, $(X^+Y_{0.5}^{4+}Z_{0.5}^{2+}T^{-4})$,$(X^{3+}T^{-3})$—but only

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[61] This is not to say there is commonly a positive correlation between phosphorus and REEs. Peraluminous hi-P granites have extremely low concentrations of REEs.

[62] Research on REE paragenesis (associations and inter-mineral developmental relationships) is on-going. As an example, noted positive associations

in REE-rich niobium-yttrium-fluorine (NYF) pegmatites as compared to REE-poor lithium-cesium-tantalum (LCT) pegmatites are with uranium, thorium, complex oxides, A- and I-type granites, and "dry" melts. (Galeschuk 2005).

[63] Organic chemists and biochemists who study the geometry of hydrocarbon polymers may know the feeling. Like SiO_4, how complicated can CH_4 get!
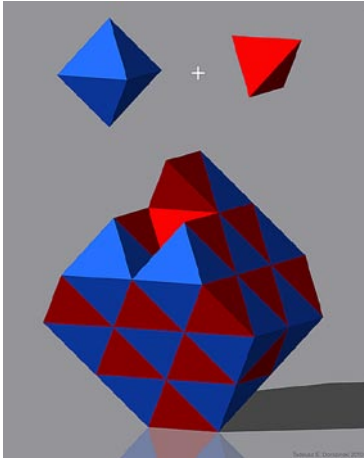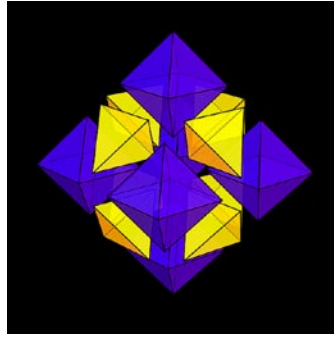
Figure 23a: A mix of tetrahedra and octahedra can fill a 3-d space, the basis of the structure of many common silicate minerals. Cubic and all parallelepiped structures can also but are less common.

Feldspars, $X^+[AlO_2(SiO_2)_3]^-$, $X^{2+}[(AlO_2)_2(SiO_2)_2]^{2-}$, have a tetrahedral lattice geometry (all-corners-linked SiO_4^{4-} and AlO_4^{5-}) without octahedra, but, nevertheless, this less-organized geometry plus the requirement for cations in the cavities to balance the charges, is still not enough to offer opportunities for REEs to be part of their structure. In part, this must be because the peraluminous (Al-rich) magmas from which feldspars form have, in aluminum, an abundance of smaller trivalent atoms that easily compete with REEs for a berth. Europium (Eu^{2+}) does however sometimes substitute for Ca^{2+} in anorthite in non-oxidizing environments.

Some clays contain small amounts of REEs, and Eu^{2+} anomalies are common, but I've not read any evidence that the REEs are there in quantity as much more than detrital particles, regardless of the type of clay (illite, smectite, or kaolinite).

reluctantly, and the flexibility in size does not extend to ions of the REEs.[64]

Quartz contains no REEs other than in inclusions.

Biotites also only allow traces of REEs, but muscovite, another mica, rather surprisingly, does sometimes contain REEs. A formula for micas that emphasizes their sandwich structure is:

$(Si_{1.5}Al^-_{0.5}O_5).Y(OH)_2.(Si_{1.5}Al^-_{0.5}O_5).K^+$
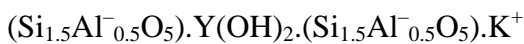
 where $Y = Al_2$ (*muscovite*); or Mg_3 (*phlogopite*, Mg-biotite); or $Fe[II]_3$ (*annite*, Fe-biotite). The capacity of muscovite to accommodate REEs is thus possibly due to the Al^{3+} ion being smaller than Mg^{2+} or Fe^{2+} ions, and only two Al ions being required for every three Mg or Fe ions.
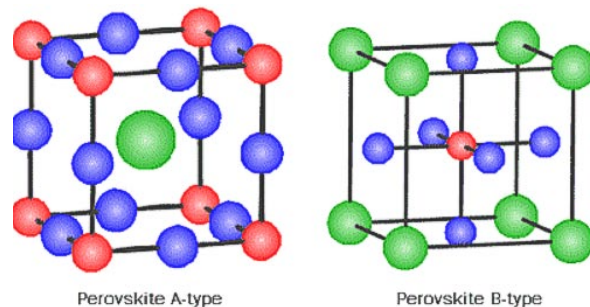

Figure 23b: Large cation green. Smaller cation red. Oxygen (or fluorine) blue.

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[64] The order of preference for the X (M2) sites in clinopyroxenes is Mg^{2+}, Fe^{2+}, Mn^{2+}, Li^+, Ca^{2+}, Na^+. For the Y (M1) sites, it is Al^{3+}, Fe^{3+}, Ti^{4+}, Cr^{3+}, V^{3+}, Ti^{3+}, Zr^{4+}, Sc^{3+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}. And for the tetrahedral sites, it is Si^{4+}, Al^{3+}, Fe^{3+}. The trivalent rare earth ions RE^{3+} radii are all >100 pm, compared to Al^{3+} 68 pm, Fe^{3+} 69pm, Cr^{3+} 76pm, V^{3+} 78 pm, and Ti^{3+} 81pm. No contest. Only scandium, a dubious REE , 89 pm makes the list.

REE-friendly silicates

The very few (and rare) silicate minerals that do accommodate REEs are silicates with large cavities. Examples are allanite with loosely bound pairs of tetrahedra (epidote group); eudialyte-eucolite with

three- and nine-fold rings of tetrahedra; garnets, which are found in metamorphic rocks, which contain a loose array of tetrahedra and octahedra;[65] and anhydrous feldspathoids and their hydrous relatives, zeolites.

Zircon, $ZrSiO_4$, contains, in addition to silicon tetrahedra, zircon triangular dodecahedra,[66] and these can accommodate large interstitial ions without excessive structural strain.[67]

Provskite is usually a titanate rather than a silicate, but some silicates (orthopyroxenes), adopt a provskite-structure at very high pressures such as exist in the lower mantle.[68] Although the pure structure is cubic, it is often stretched or squashed. Provskites can accommodate large ions, and be a rich source of REEs.

Feldspathoids and zeolites

Feldspathoids and their hydrous relatives, zeolites, are framework alumosilicates like feldspars, but because they contain less silica (they are undersaturated), rings of silica tetrahedra, which are restricted to rings of four or eight in feldspars, can be many different and larger sizes in feldspathoids and zeolites. The more open framework and large cavities of these minerals allow for the accommodation of larger cations
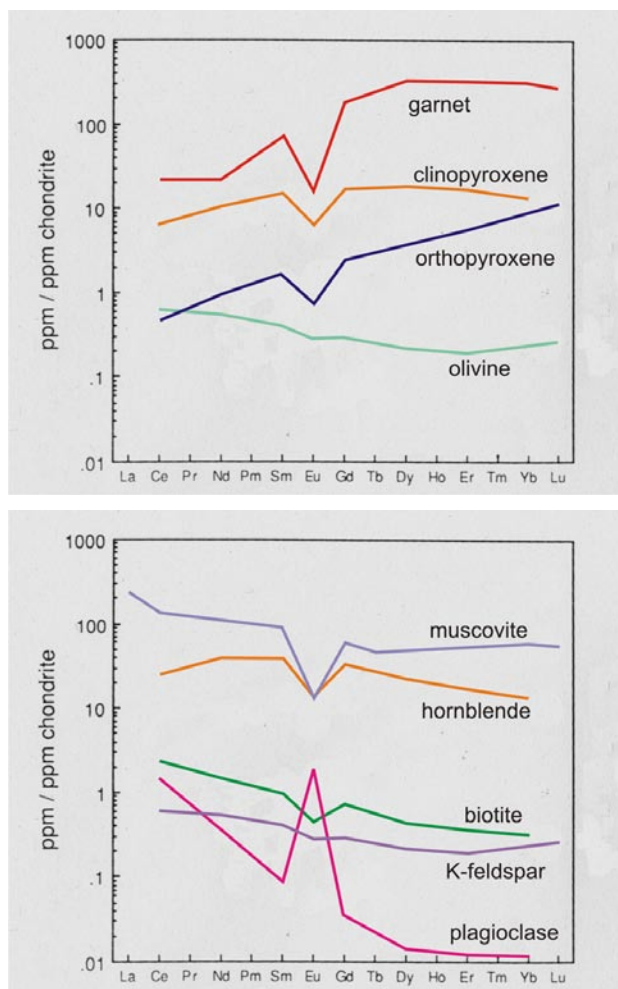

Figure 24: REE concentration in some common silicate minerals. In general, mafic minerals formed at high pressure have a compact structure that leaves little room for REEs, while felsic minerals formed at low pressure, or even at the earth's surface, have looser structures and are more likely to be able to accomodate REEs and other "nobody wants us" rare elements.

Adapted from Taylor 1988.

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[65] Yttrium iron garnet (YIGs) doped with REEs widely used in the electronics industry are synthetic but with the structure of grossular-garnet.

[66] Don't ask me to draw one—life would be so much simpler if we lived in a 2-d world. Rhombic dodecahedral honeycombs are duals of tetrahedral-octahedral (cuboctahedral) honeycombs.

[67] The ionic radius of Zr^{+4} is 86 pm compared to Si^{+4}'s 54 pm.

[68] Rhombic dodecahedra are related to face-centred cubic sphere packing, which is the densest possible packing of equal spheres.

than the feldspars and even of interstitial anions and anion groups (e.g. Cl^-, CO_3^{2-}, SO_4^{2-}, NH_4^+, and, in zeolites, H_2O).[69]

Significant concentrations of LREEs are often associated with feldspathoid minerals that form when there is a lack of silica, an over-abundance of alkali

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[69] Wenk, HR. and Bulakh, A. 2004. *Minerals—their constitution and origin*, Cambridge University Press, Chapter 29.

elements (Na and K), and insufficient aluminum to make feldspars.

The predominant feldspathoid constituent in these environments is nepheline,[70] or less often the sodalite group of minerals,[71] and analcime,[72] but the detailed mineralogy of those peralkaline undersaturated minerals that are of economic interest is challenging, to put it mildly. For a start, there are a lot of them. Yakovenchuk et al. (2005) list forty-five REE minerals, not including those where REEs substitute for other cations, throughout some forty different rock types in just one complex alone (Khibiny, Russia, not far from the border with Finland).[73]

REE-carbonates

The well-known mineralogist's bible, *The Rock-forming Minerals*,[74] devotes 518 pages to silicate minerals compared to 141 to the non-silicates, a reflection obviously of the importance of silicon in

geochemistry. However, when it comes to considering the occurrence of REEs in rocks, carbonates and fluorocarbonates found in silica-undersaturated deposits attract a great deal of attention. Carbon has also become the focus of many petrologists with the discovery that there is no remaining doubt that carbonates form magmas within the deep mantle, and that a great deal of the earth's crust is, somewhat mysteriously, severely depleted in carbon.[75]

Given that carbon is in the same group as silicon, one might expect there to be an extensive group of minerals based on tetrahedron-shaped CO_4^{4-} ions. Computer simulations (with supporting experimental evidence) have indicated that $MgCO_3$ can indeed adopt a metastable pyroxene-like structure, and $CaCO_3$ can adopt a metastable β-cristobalite-like-tetrahedral-framework structure, but only at very high pressures (Jones 2013). The possible role of such polymers in deep-mantle geochemistry is at present only poorly understood.

Because carbon atoms are smaller than silicon atoms, and because carbon has a higher electronegativity ($\chi = 2.6$) compared to silicon ($\chi = 1.9$), it forms CO_3^{2-} ions at surface temperatures and pressures. Unlike in the tetrahedral SiO_4^{4-} ion, the trigonal pyramidal CO_3^{2-} contains intra-ion bonds that leave no unpaired orbitals available for inter-ion covalent bonding, and hence the ions do not polymerize.

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[70] Nepheline is $Na_3K[AlSiO_4]_4$, but end members $NaAlSiO_4$ and $KAlSiO_4$ (kaliophilite) are known.

[71] Sodalite is $Na_4[AlSiO_4]_3Cl$. The group also includes haüyne $Na_3Ca[AlSiO_4]_3SO_4$, lazurite $Na_3Ca[AlSiO_4]_3S$, and several others with names almost impossible to pronounce and formula almost impossible to remember.

[72] Analcime, $Na[Al_{0.5}SiO_3]_2.H_2O$, is technically a zeolite, but its structure and chemistry is more like that of a feldspathoid.

[73] Chakhmouradian AR. & Zaitsev AN. 2012. They note that names like lujavrite, melteigite, and ijolite would perplex even a seasoned petrographer. Other types of REE deposit also contain a plethora of mineral types, a consequence of course of the REEs being among a variety of incompatible "nobody wants us" elements. A paper on alkaline granite-syenite deposits by Salvi & William-Jones (2005) mentions 43 minerals, many of which like naujakasite, steenstrupine, and mosandrite, contain an REE.

[74] Deer WA., Howie, RA., & Zussman, J. 1992. *The Rock-forming Minerals*, Prentice Hall. pp.696.

[75] Check out the Deep Carbon Observatory website: https://dco.gl.ciw.edu/
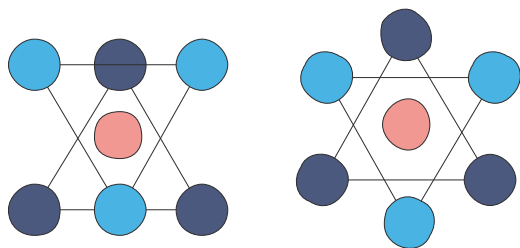
Figure 25: The structure of carbonates can resemble that of calcite (left) or aragonite (right), both shown here in super-simplified undistorted form [don't quote me].

The lighter blue spheres are CO_3^{2-} ions in one sheet; the darker blue spheres are also CO_3^{2-} ions lying in sheets above and below the plane of the paper. Cations, the pink spheres, link six O^{2-} ions together $Ca^{2+}O_3^{-2/3}C^{4+}O_3^{-4/3}$; they are not interstitial as in silicates) and lie between the stacked sheets, approximately mid-way in calcite and off-vertical-centre in aragonite. Larger cations prefer the aragonite structure; smaller ones the calcite structure.

At constant P, aragonite becomes calcite with increasing T; but at constant T, the reverse is true with increasing P. REEs (and other heavy ions) disperse within calcite (and dolomite) in cooling magmas, but also form their own aragonite-type isomorphs, in part because REE (and other metal) cations are unlike Ca^{2+} and Mg^{2+} in size and charge.

Carbonate minerals of biogenic origin, principally limestone and dolomite, do not contain only traces of REEs—the REE concentration in marine carbonates is actually lower than in detrital sediments,[76] and, except for a lack of cerium depletion, reflects the distribution of REEs in the sea.[77]

Despite the lack of REE concentration in biogenic carbonates, carbonatites (rocks containing >50 vol.% carbonate minerals and < 20 vol.% quartz) show no such lack of REEs. A significant share of these REEs is dispersed among the major carbonate minerals (mostly calcite and dolomite); however, there is also significant concentration in a plethora of associated and little-known REE-rich carbonates, fluorocarbonates, phosphates, sulphates, and silicates.[78]

Carbonatites deposits are readily altered hydrothermally, and by weathering, and ultimately by mass fractionation—the formation of placers and heavy mineral sands by rivers and waves along the shore. In extraordinarily rich deposits, more than one such process may have been involved in their petrogenesis.

Geochemically, carbonatites often contain positive anomalies in large ions such as strontium, barium, lead, and the LREEs, which would be consistent with them being contained in aragonite-type carbonate minerals (see Figure 25).

Carbonatite environments that include water are alkaline with their pH being tightly-controlled by carbonate buffering.[79] Such environments are also

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[76] The principal source of ocean sediment is the continents. Oceanic crust is poor in REEs relative to terrigenous crust. As sea floors spread, they sweep REEs towards the continents and subduction zones for recycling. (Haskin 1979, pp.12 & 16).

[77] Cerium depletion in seawater is possibly due to selective adsorption by ferromanganese modules. Marine phosphates also have low chondritic concentrations of REEs.

[78] A partial list of these is burbankite $(Na,Ca)_3(Sr,Ba,Ce)_3(CO_3)_5$; carbocernaite $(Ca,Na)(Sr,Ba,Ce)(CO_3)_2$; ancylite-Ce $SrCe(CO_3)_2OH.H_2O$; synchysite-Ce $CaCe(CO_3)_2F$; bastnäsite $(Ce,La,Y)CO_3F$; strontianite, $SrCO_3$; barite $BaSO_4$; and cerrusite $PbCO_3$.

[79] Too acidic? then:
$CO_3^{2-} + H^+ \rightarrow HCO_3^-$
$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$
$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$

Too alkaline? then:
$CO_2 + OH^- \rightarrow HCO_3^-$
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

most often oxidizing by contact with the atmosphere.[80] Many metals, including REEs, form relatively insoluble and hence immobile minerals in these conditions. These minerals include carbonates, oxide/hydroxides, fluorides, and fluorophosphates (commonly fluorapatite, $Ca_5(PO_4)_3F$).

REE-phosphates

High-polymetric phosphates containing several hundred tetrahedral PO_4^{3-} ions are known to biochemists, but, as far as I am aware, there are no minerals that incorporate such structures.

In magmas, phosphorous concentration sometimes shows strong negative correlation with REEs; yet, in hydrous minerals at the surface, the reverse may be the case. Possibly (my speculation) this is due to the availability near the surface of, depending on pH, HPO_4^{2-} and $H_2PO_4^{-}$ ions for making complex polymetallic minerals. ◊

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[80] But reducing environments in rocks at depth by virtue of $CO_2 + 4OH^- \rightarrow CH_4 + 4e^- + 3O_2$.

REE petrography

In this section, I want to look at the overall distribution of REE minerals in various types of rock, before going on to discuss, in the following section, the petrogenesis of those rocks that are of special interest.

REE-rich rocks occur in a variety of different geological settings, not all well-understood. However, no matter what their provenance, REE deposits that are of economic interest all involve some sort of additional evolutionary process to concentrate them.

These secondary, and even tertiary, processes are themselves varied and complicated, and so it is just not feasible in a report of this nature to describe them all in detail. So, just to be clear, when I talk about "high REE concentrations" in this section, I am rarely implying that these concentrations are anywhere near high enough to make the rock under discussion worth exploiting.

Primary processes in the creation of REE-rich magmas and hence rocks involve:

—tectonic activity and intra-tectonic-plate (hot spot) volcanism;

—magma sourcing (deep or shallow mantle, with or without crustal contributions, magma mixing)

—fractional crystallization in magmas;

—the effect of fluxes (mainly H_2O and CO_2, but also other volatiles lost in eruptive degassing);

—element partitioning during unmixing of immiscible melts, and;

—partial melting (incorporation of minerals from country rock into intrusive magmas).

All of these I will touch on in the section following this one.

Secondary and tertiary processes include:

—metasomatism: chemical alteration by hydrothermal and other fluids;[81]

—metamorphic changes (alteration of the rock through temperature and pressure without re-forming liquid magma);

—weathering (metamorphism through contact with the atmosphere resulting in concentration in saprolites and laterites; oxidation/reduction by groundwater), and;

—mass fractionation (which for REEs is not unlike isotopic fractionation).
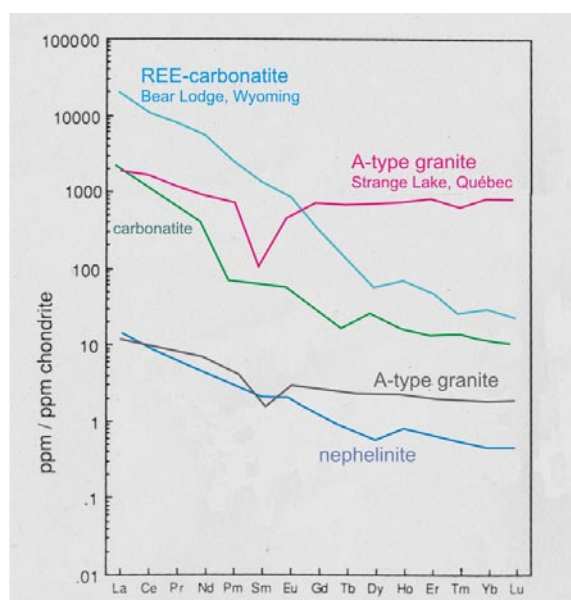
Figure 26: Rock types with ore-grade concentrations of REEs (carbonatites, A-type granites, etc.) don't all come that way. Compare for example average carbonatite concentrations with REE-rich carbonatite concentrations. Secondary processes are always needed to produce REE ores.

Re-drawn from Chakhmouradian 2012

[81] Hypogene mineralization is mainly the result of ascending fluids; supergene (hypergene) mineralization is mainly the result of descending fluids

Some concentrations of REEs are the result of inclusive processes; and some are the result of exclusive processes. A good example of the latter is REE-rich pegmatic rocks in granitic, granodioritic, and peraluminous rocks. These types of incompatible-element-rich pegmatite are there, primarily, because the host rock is correspondingly depleted in such elements.

Rocks and unconsolidated sediments that do contain concentrations of REEs high enough to be of economic or potential economic interest include:

- —foidal syenites (peralkaline undersaturated rocks)
- —peralkaline granitic rocks
- —granitic pegmatites (common but usually too low grade or too small to be commercially exploited)
- —vein deposits (like pegmatites, typically too small, but there are exceptions in dykes, veinlet swarms, and stockworks) (Castor 2006)
- —carbonatites (magmatic, metasomatic, and supergene mineralization, sometimes in multiple stages)
- —hydrothermal deposits with anomalous concentrations of REEs including iron-oxide deposits (with REEs as by-products)
- —phosphate and fluorspar deposits (with REEs as potential by-products, though the economics of this are dubious)
- —placer, paleoplacer, heavy sand, saprolitic, and laterite deposits; and paleo clastic sedimentary rocks derived from such deposits.

However, nothing is simple in these matters—every author will have their own list. All the above "types" come in,

several, sometimes very different, "subtypes", and the types are not mutually exclusive—they're not orthogonal as a mathematician might say. For example, the Bayan Obo deposits in China, which are the world's largest REE resource, are hosted by dolomite (a carbonate); are a major iron-oxide deposit; and are rich in monazite—which is a phosphate. However, before haranguing nature for being so complicated, one should remember that the early Swedish chemists used, not just a handful of steps, but many thousands of steps to isolate REEs from one another, and even today, modern methods of separation still involve hundreds of automated and repetitive stages.

Chondrite norm

Distributions of the REEs in rocks (usually meaning only the lanthanides) is commonly expressed, not in absolute parts per million (ppm), but in comparison with their concentrations in chondrites, a class of meteorites that is believed to come closest to retaining the nonvolatile elements of the solar system in their primitive abundances.[82]

Chondrite normalized distributions of REEs give an easily- and widely-used measure of REE concentrations in samples of magmas, rocks, and minerals. The trend of the concentrations with atomic number from LREEs to HREEs are also an invaluable source of petrological information. Normalization also

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[82] Nobody knows what the original composition of the earth was, but chondrite composition is a commonly used standard (let's hope it's a valid one). It matches the composition of the sun's atmosphere and interstellar dust clouds. Chondrite norms can be found in (Sun & McDonough 1989) and (McDonough & Sun 1995).

eliminates the distracting Oddo-Hawkins effect (see Figure 27).

The earth's crust

As noted already, fractionation of REEs is always a multi-step process, and it begins with the enrichment of the earth's continental crust relative to its core and mantle. Figure 27 illustrates how substantial this enrichment might be, varying in this example, from 97 for lanthanum to 14 for lutetium.[83]

REEs in igneous rocks

Igneous rocks include:

—volcanic rocks (extrusives–high temperature and high
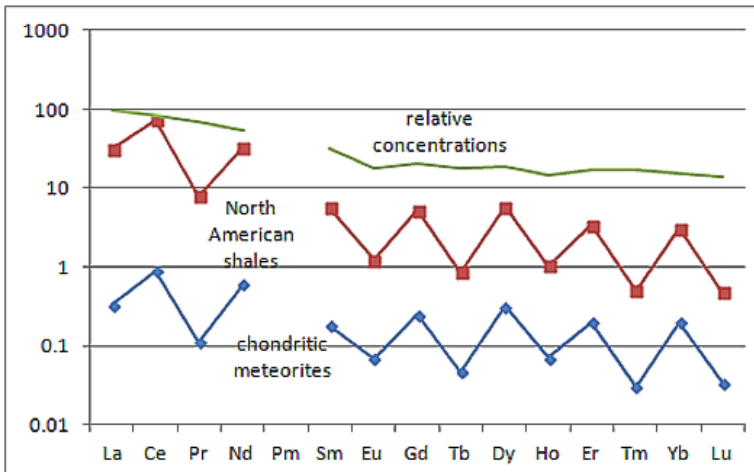
Figure 27: Concentration of REEs (ppm) in chondrites (N=9) and North American shales (N=40); and the relative concentrations shales/chondrites.

Atomic nucleii with even numbers of protons have higher binding energies (are more stable) than those with odd numbers; hence the sawteeth (the Oddo-Harkins effect). Normalization eliminates this effect.
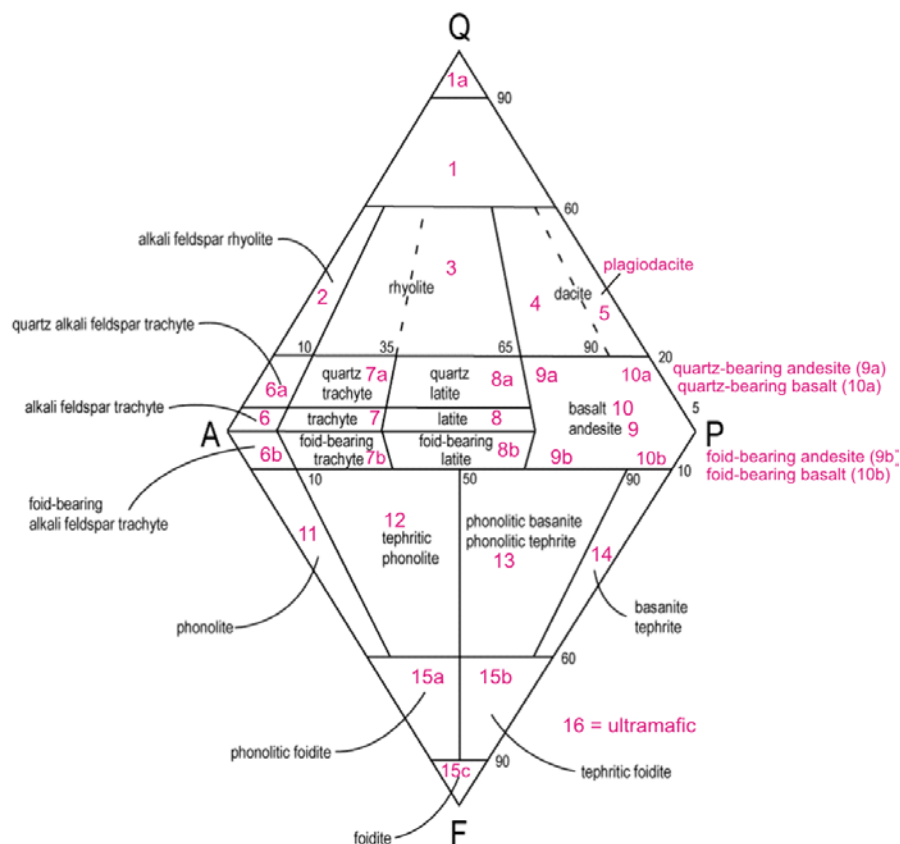
Haskin 1979

Figure 28: QAPF diagram for volcanic (phaneritic) rocks. Mafic minerals, vol.% < 90.

pressure)

—plutonic rocks (intrusives—high temperature and low pressure)

—hypabyssal (veins and sills—high temperature and medium pressure).

Because of the incompatibility of REEs with many rock-forming minerals, their concentration in common rocks is often controlled by the concentration of tiny amounts of unusual, and frequently overlooked, REE-rich minerals. This is especially true of the LREEs in felsic rocks.[84]

Classifying volcanic rocks

Most readers will have some familiarity with the top half of QAPF diagrams, especially the righthand side of the top half, but REE mineralogy, petrography, and petrology frequently requires attention to be paid to the the bottom half and the lefthand side, so a review may be in order.

In Figure 28:

Q stands for quartz;

A stands for alkali feldspar (K-feldspars plus albite if it is pure and clearly part of a Na/K assembly of minerals rather than a Na/Ca assembly);

P stands for plagioclase (including albite if it is clearly an end-member, and not a K-feldspar associate); and

F stands for foid (rocks containing >60% feldspathoids).

The combination of upper and lower triangles is only possible because quartz and feldspathoids never occur together. Within each triangle, QAP and FPA, the combinations, in volume (modal)

percentages are normalized to add up to 100%.

This particular version of the QAPF diagram is for volcanic rocks in which the mineral crystals are sufficiently large for them to be identified.

Why are feldspathoids and quartz incompatible? The answer goes something like this.

Because of the abundance of oxygen in the earth's atmosphere, terrigenous rocks are either in an oxidized state, or are on their way to becoming oxidized through weathering. An oxidizing environment is one where electron-acceptors outnumber electron-donors.[85]

Oxygen is only one of many oxidizers—fluorine is an even more powerful oxidizer than oxygen. Deep below ground in the mantle, where oxygen is scarce (oxygen frugacity, $f\,O_2$, is low), silica (SiO_2) takes on the role of oxygen. Thus, on the surface we don't expect to see FeO because of the oxidizing reactions:

$6FeO + O_2 \rightarrow 2FeO.Fe_2O_3$
ferrous oxide → magnetite

$4FeO.Fe_2O_3 + O_2 \rightarrow 6Fe_2O_3$
magnetite → hematite

Hematite is more common than magnetite in weathered rocks.

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[84] Miller CF. & Mittelfehldt 1982. *Depletion of light rare-earth elements in felsic magmas*, Geology 1982;**10**; pp.129-133.

[85] The reverse, electron-donors outnumber electron-acceptors, is a reducing environment. Just as alkaline (basic) environments are ones where proton-acceptors outnumber proton-donors, so are acidic environments ones where proton-donors outnumber proton-acceptors.

Extreme reducing and acidic conditions cannot co-exist because the donation of both electrons and protons generates hydrogen ($2e^- + 2H^+ \rightarrow H_2$). It is similarly rarely possible for extreme oxidizing and alkaline conditions to co-exist because hydroxyl ions donate protons and electrons and generate free oxygen ($2OH^- \rightarrow 2H^+ + 4e^- + O_2$).

So in the mantle, we don't expect to see much $KAlSiO_4$ because of the oxidizing reactions:

$KAlSiO_4 + SiO_2 \rightarrow KAlSi_2O_6$
kaliophilite $\rightarrow$ leucite

$KAlSi_2O_6 + SiO_2 \rightarrow KAlSi_3O_8$
leucite $\rightarrow$ orthoclase
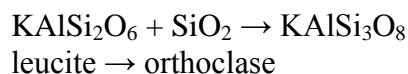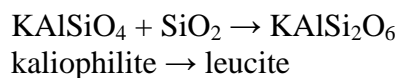
Orthoclase is far more common than leucite in magmas rich in quartz.

Feldspathoids like nepheline, kaliophilite, and leucite cannot co-exist with quartz, essentially because quartz is an oxidizer. Carbonatite environments also are reducing environments away from the atmosphere.

Why do undersaturated foid rocks contain more REEs than saturated granitic rocks? Part of the answer is that feldpathoids have a more open structure than feldspars, and so are able to accommodate large, highly-charged cations more easily.

Another part of the answer, is that undersaturated (alkaline) magmas have lower melting points and lower viscosity than silicic magmas, especially when they contain CO_2 and H_2O as they often do, so they are the last to crystallize, and have travelled furthest from the source when they do so, thereby providing a haven for incompatible elements.

Yet, another part of the answer is that although foid rocks tend to have only a few *essential* minerals, they have very large numbers of accessory minerals, among which are some that are REE-friendly. Some agpaitic rocks particularly contain hundreds of different minerals (Sørenson 1997).

Examples of volcanic rocks containing feldspathoids with their essential minerals are:

ultramafic: <u>melilitite</u> (melilite,[86] acmite-augite, olivine), <u>carbonatite</u> (calcite or dolomite);

mafic: <u>nephelinite</u> (nepheline), <u>leucitite</u> (leucite), <u>tephrite</u> (plagioclase, clinopyroxene, nepheline or leucite), <u>basanite</u> (plagioclase, clinopyroxene, nepheline or leucite, olivine);

intermediate: <u>phonolite</u> (sanidine, nepheline, clinopyroxene or sodic amphibole).

And that is about it.[87]

Accessories however include aenigmatite, albite, analcime, analcite, anorthoclase, apatite, augite, barite, cancrinite, carbonate complexes, chromite, fluorite, haüyne, hornblende (brown), ilmenite, magnetite,[88] melanite, melanite garnet. monazite, niobite, noselite,[89] olivine, perovskite, phlogopite, picotite spinel, plagioclase, pyrite, pyrochlore, sodalite, titaniferous biotite, titanite, zeolites, and *et cetera*, as the reference books say.

Classifying plutonic rocks

Figure 29 shows the QAPF diagram for plutonic (intrusive) rocks. Examples of intrusive rocks containing feldspathoids fall into the general category of <u>feldspathoid syenites</u>, which are mafic rocks with, as essential minerals, alkaline

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[86] Melilite is $(Ca,Na)_2(Al,Mg,Fe^{3+})(Si,Al)_2O_7$. There are several other rare minerals with the same structure, some containing beryllium. However, they are not noted for including REEs.

[87] Note that although feldspathoids and quartz do not co-exist, mixes of feldspathoids and feldspars are common.

[88] The presence of magnetite $(FeO.Fe_2O_3)$ rather than hematite (Fe_2O_3) is interesting as it indicates the chemical environment the minerals formed was not strongly oxidizing. For discussion, see: http://en.wikipedia.org/wiki/Mineral_redox_buffer

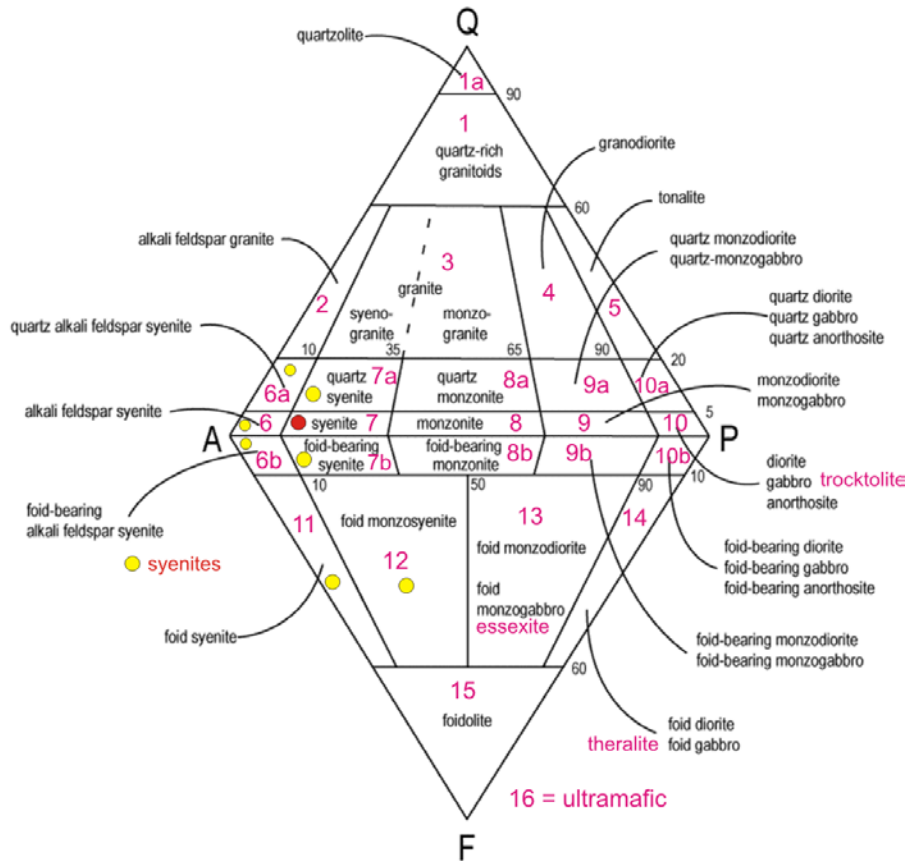[89] Noselite (nosean) is $Na_8(Al_6Si_6O_{24})(SO_4)$.

Figure 29: QAPF diagram for plutonic rocks. Mafic minerals, vol.% < 90. Rocks marked with a yellow dot are often just called "syenites" (*sensu lato*); the rock marked with a red dot is "syenite" (*sensu stricto*). Alkaline syenites can be important hosts of REE mineral.

feldspars (with or without albite) and nepheline with sodalite or cancrinite[90].

The feldspathoid syenites have a long list of accessory minerals, some with high REE content, including plagioclase, analcite, acmite, sodic amphibole, aeigmatite, magnetite, biotite, fluorite, eudialyte, astrophyllite, and others.

Theralite is the intrusive equivalent of basanite, which is a foidal basalt containing calcic-plagioclase, pyroxene, olivine, and nepheline.

Essexite (more formally known as foid monzogabbro or foid monzodiorite) contains nepheline and plagioclase with minor alkali feldspar, pyroxene, hornblende, and biotite. It is a product of very light (<10%) partial melting, and the near-equivalent of an alkali basalt.

Other foidal rock types, mostly syenites (*sensu lato*) mentioned by specialists and sometimes invoking "did you spell it correctly?" responses, are footnoted here.[91]

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[90] Cancrinite is a complex carbonate, $Na_6Ca_2[(CO_3)_2|Al_6Si_6O_{24}].2H_2O$.

[91] Foyaite (nepheline syenite rich in K-feldspar; ijolite (mainly nepheline and aegirine); jacupirangite (ultramafic ijolite dominated by

Agpaitic rocks

Geologists who specialize in the "-APF" part of the QAPF diagram, particularly those interested in commodity rocks, often use the term "agpaitic". These are those peralkaline nepheline syenites and phonolites that do contain complex silicates of Zr, Ti, REEs, and F and other volatiles. I shall have more to say on their petrogenesis further on in the article.

Types of granites

Granites (meaning granitoids in general) are often classified in field studies into types depending on their geochemistry, intrusive settings, isotopic signatures, and mineralogy. Of these, A-type granites are most often of interest when it comes to REE concentrations.

I-type (igneous) granites are taken to be from the melting of pre-existing (protolithic) unweathered igneous rocks. They contain amphiboles (hornblende) as their mafic mineral, are enriched in sodium and calcium, and have a geochemical signature similar to that of basalts.

S-type (sedimentary) granites are from melted sedimentary rocks or their metamorphic equivalents. They are rich in muscovite and biotite, depleted in sodium, and enriched in aluminum. They are commonly associated with subduction zones.

M-type (mantle) granites are rarer and are thought to have evolved directly from the melting of mafic rocks originally from deep in the mantle. They occur in island arc settings.

A-type (anorogenic) granites are I-type granites that contain alkali feldspars and have iron-rich mafic mineralogy, high LILE and HFSE abundances, and pronounced anomalies due to high degrees of mineral fractionation. They are found in intra-continental (anorogenic) settings, commonly those that are or were involved in continental rifting. Although many petrogenetic models imply a crustal derivation of these granites, isotopic evidence points to there being a large mantle input.[92]

Despite widespread usage, a major problem with the alphabetical classification of granites is that it carries the assumption that individual granitic rocks have a simple source, and that this source can be readily identified from the chemistry of the rocks. In actuality, granites rarely come from single sources, but instead are mixtures of mantle-derived mafic melts and melts of crustal rocks that may or may not contain meta-sedimentary components.[93]

The potassium-calcium connection

What is interesting about the lower half of the QAPF diagram—and is not in my experience commonly commented on—is that there is no feldspathoid equivalent of anorthite, as there is for albite (nepheline) and K-feldspar (leucite). The calcic-rock theralite—the rough equivalent of quartz-

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titanaugite with minor nepheline); kakorokite (eudyalite-bearing nepheline syenite); khibinites (coarse-grained nepheline syenites); lujavrite (melanocratic nepheline syenite); malignite (nepheline syenite rich in aegirine and orthoclase); melteigite (mafic ijolite with green pyroxene); naujaite (sodalite-rich nepheline syenite); pulaskite (nepheline-bearing alkali feldspar syenite); rischorrite (K-rich nepheline syenite); urtite: (leucocratic ijolite very rich in nepheline).

[92] Bonin, B. 2007. *A-type granites and related rocks*, Lithos, **97** (1–2), pp.1–29.

[93] Frost BR. et al. 2001. *A Geochemical Classification for Granitic Rocks*, Journal of Petrology, **42**(11), pp.2033–2048.

rich tonalite—is only calcic by virtue of its content of plagioclase (usually labradorite, 50–70 %An). The implied left-right symmetry of the diagram is thus deceptive. Practically all feldspathoid rocks (foidalites and syenites) contain alkali feldspathoid minerals,[94] not calcic-ones, unless one looks at rare sulphates and carbonates.

Seen with this mind, it is perhaps not surprising that REE-rich minerals are associated with potassium-rich undersaturated rocks (alkali syenites) and complexes. Potassium ions particularly are big; and K-rich melts have a low melting point—recall the Bowen reaction series with K-feldspar, muscovite, and quartz at the bottom.

The petrogenesis of alkaline, peralkaline, and ultrapotassic (molar K/Na>3) rocks is thus clearly of interest in studying the the petrogenesis of REE ores.

The aluminum connection

The differences between feldspars and feldspathoids hinges, not just on whether or not there is abundant quartz present in the magmas from which they crystallize, but on the relative abundance of aluminum. Petrologists make use of many indices in their efforts to classify the various rocks on which their interest is focussed, but one relevant basic index applicable to studies of all alkaline rocks is the aluminum saturation index (ASI). The definition of ASI that I prefer is:[95]

$Al_2O_3/(Na_2O + K_2O + CaO)$
% molar proportions

Figure 30: Classifications of rocks based on the aluminum saturation index (ASI).

Ca in apatite not included. The ASI of feldspars and feldspathoids is 1.

The use of the ASI to classify rocks as peraluminous (ASI>1), metaluminous (ASI<1 only with Ca included), peralkaline (ASI<1 without Ca), and perpotassic (ASI<1 with K alone) is summed up in Figure 30.[96]

Combining the ASI with a silica-saturation index has been done of course [97] but it becomes more complicated and one can

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[94] Rocks of this type containing potassium particularly are foyaite and kalsilite syenites (rischorrites).

[95] This avoids "finger-trouble" that might occur if you were to use % elements. The ratio would then be 1:1 for alkali feldspars, but 2:1 for anorthite.

[96] Found originally on the web, but I added perpotassic. I guess we could also take "peralkaline" to mean "apoaluminous", ASI<1, too little alumina to make feldpars.

[97] Frost BR.& Frost CD. 2008 (online). *A Geochemical Classification for Feldspathic Igneous Rocks*, Journal of Petrology, **49**(11), pp.1955–1969.

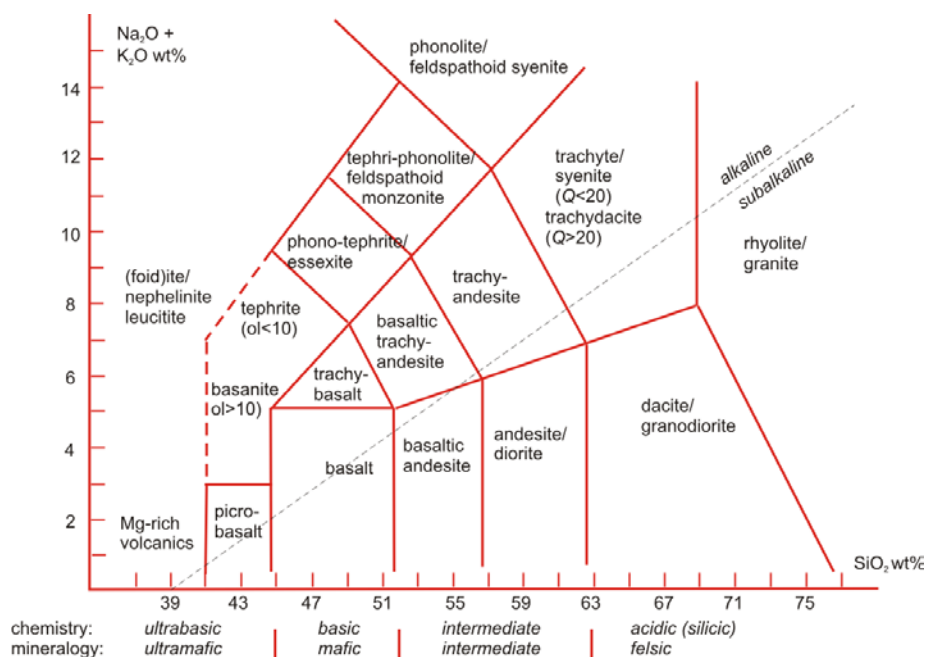Figure 31: TAS (total alkali silica) diagram based on whole rock geochemical analysis. These diagrams are intended to use for aphanitic magmas for which modal analysis (mineral content) is not possible or even meaningful. However, they are used, as here, to indicate the rock types that crystallize from the magmas.

easily use the presence or absence of quartz as an indicator.[98]

In principle, given three classes of aluminous rocks and two of silicate rocks (saturated and unsaturated), there should be six classes of aluminosilicate rocks. In practice, there are only five as peraluminous rocks are almost never unsaturated. The five are thus unsaturated and quartz-bearing peralkaline (alumina deficient, Roux 1975), quartz-bearing peraluminous (alkali deficient), and unsaturated and quartz-bearing metaluminous (nominally alumina deficient but with Fe^{3+} substitution).

The evolution of alkaline rocks

How different rocks relate to one another is probably a familiar topic when it comes to the evolution of, say, basalt magmas through andesine magmas to rhyolite magmas, as the proportion of silica in the magma increases as minerals crystallize, but maybe less so for alkaline (silica-undersaturated) rocks. Since undersaturated rocks play such an important role in the petrogenesis of many REE-rich deposits, I have included the pertinent TAS diagram here—in Figure 31, TA is total wt.% of alkali (Na_2O+K_2O) and S is wt.% of silica (SiO_2).

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[98] You have to be careful when interpreting changes in indices. Suppose you have a rock containing 40 units of A and 10 units of B. Then the A-index is 40/50 = 0.8 and the B-index is 10/50 = 0.2. If you now take out a mineral containing 5 units each of A and B, then the new A-index is 35/40 = 0.88 and the new B- index is 5/40 = 0.13. Even though you take out equal amounts, the index of the mineral with the larger presence, A, goes up and the index of the mineral with the smaller presence, B, goes down. Removing feldspar, which has an ASI=1, reduces the ASI of whole rocks with ASI<1, but raises the ASI of whole rocks with ASI>1.

Figure 32 shows the evolutionary paths of tholeiitic (subalkaline), calc-alkaline, and the less common silica-undersaturated / alkaline/ peralkaline magmas, and Figure 34 shows a few of the minerals that the various rock types contain.

The following is from (Sørensen 1997) with my annotations in []:

Figure 32: TAS (total alkali silica) magma evolutionary paths through fractional crystallization. The lower path is the tholeiitic series; the middle path the calc-alkaline series; and the upper path is the silica-undersaturated / alkaline / peralkaline series.

Alkaline magmas have solidification temperatures as low as 500 to 400°C and are often accompanied by a gas phase rich in methane, [which is indicative of a reducing environment], and sodium-rich fluids as indicated by the presence of minerals such as ussingite and villiaumite,[99] and of pegmatites and hydrothermal veins rich in sodium and rare and volatile elements.

Agpaitic nepheline syenites are considered to have been formed by consolidation of melts oversaturated in alkalis, under conditions preventing the volatiles from escaping. These melts have been derived by extreme fractionation processes in alkali basaltic or nephelinitic magmas.

The main stage of crystallization of the melts is characterized by minerals such as nepheline (sometimes also sodalite), alkali feldspars, arfvedsonite, aegirine,[100] and eudialyte, but the most highly developed, hyperagpaitic lujavrites of the Ilímaussaq complex [in Greenland] have been formed from melts with extreme concentrations of sodium and volatiles resulting in the formation of naujakasite [101] instead of nepheline, ussingite instead of sodalite and alkali feldspars, and steenstrupine[102] instead of eudialyte.

During the late stages of crystallization, sodium-rich fluids are the cause of late- and postmagmatic alteration and of the formation of hydrothermal mineralizations. The late stages are characterized by water-soluble sodium-rich minerals of which more than 80 have been found in the Khibina and Lovozero complexes.

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[99] Ussingite is $NaAlSi_3O_8.NaOH$; villiaumite is NaF.

[100] Arfvedsonite is $Na_3Fe_5Si_8O_{22}(OH)_2$; aegirine is $NaFeSi_2O_6$.

[101] Naujakasite is $Na_6(Fe,Mn)Al_4Si_8O_{26}$.

[102] Steenstrupine-(Ce) is $Na_{14}Mn_2(Mn,Fe)_2Ce_6(Zr,Th)(Si_6O_{18})_2(PO_4)_6(HPO_4)(OH)_2.2H_2O$.
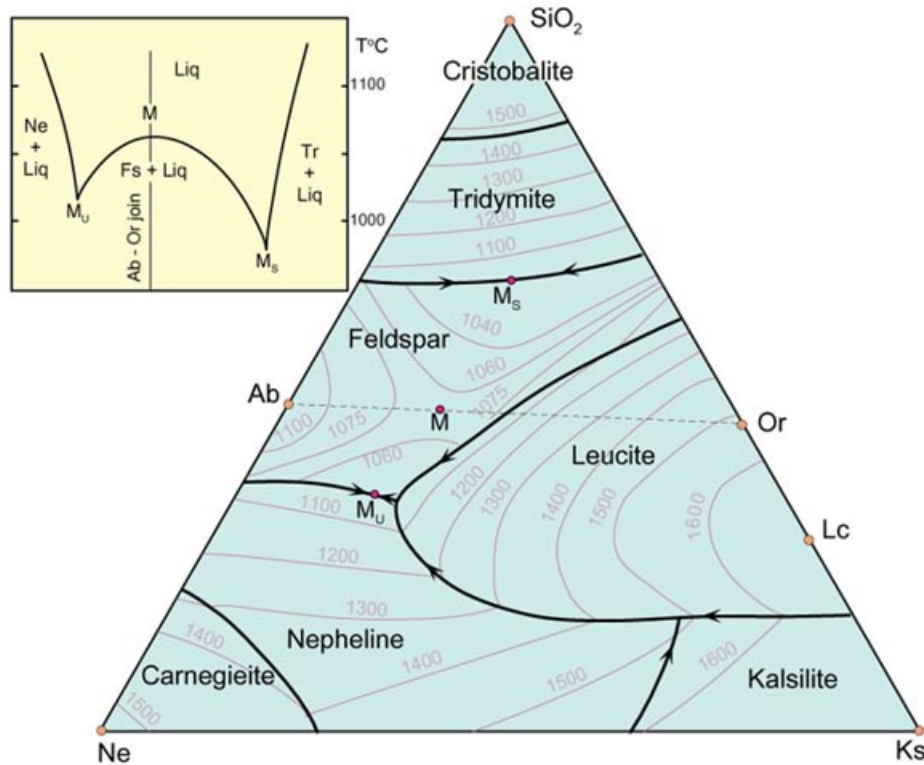
Figure 33: Phase diagram for SiO_2-nepheline [(Na,K)AlSiO$_4$]-kalisilite (KAlSiO$_4$)) at 0.1 MPa. As temperatures of a magma falls, the composition converges on M_U or M_S. M_U represents a typical alkali-feldspar-nepheline-leucite phonolite; and M_S represents a typical saturated alkali feldspar-quartz rhyolite. Tridymite is simply a high-temperature polymorph of quartz. Leucite is (KAlSi$_2$O$_6$) a less-undersaturated kalsitite. Carnegeite is a high-temperature polymorph of sodium-rich nepheline NaAlSiO$_4$.

There is also a thermal barrier between albite and orthocite-leucite. Trachytic magmas (the middle arrow in Figure 32) that evolve close to the line joining Ab-Ob may become very different magmas depending on which path the fractionating feldspars decide to follow.

<div align="right">Winter 2010, Fig. 19.7</div>
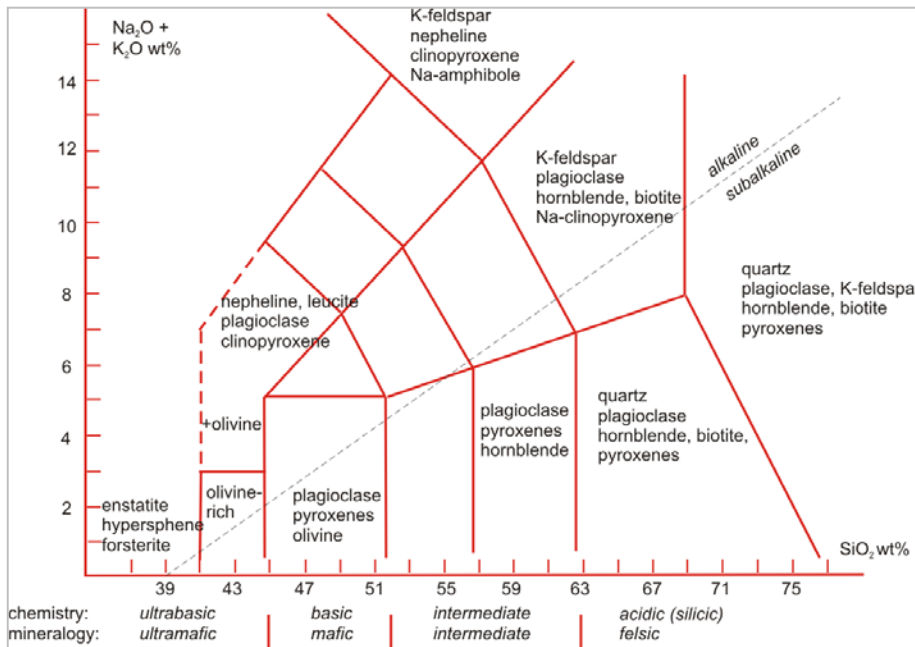
Figure 34: TAS (total alkali silica) paths. The lower arrow shown in Figure 32 closely follows the left-hand side of Bowen's Reaction Series: olivine→pyroxene→amphibole→biotite→K-feldpar, muscovite, quartz. Correspondence of the upper two arrows with the right-hand side of Bowen's Reaction Series is not so palpable, but similarities are apparent.

Group II kimberlites (or orangeites) are very mafic rocks that possibly have had incompatible elements added by magma mixing. They contain phlogopite.

Lamprophyre is a grab-bag name for a variety of rare porphyritic rocks that are otherwise difficult to classify. They typically occur as minor hypabyssal intrusions (sills, dikes, stockworks, volcanic necks). Minette lamprophyres are rich in biotite, orthoclase, and sometimes REEs. Some lamprophyres are associated with subduction zones, others with intraplate rift environments along with other alkaline-carbonate complexes.

Lamproites, class II kimberlites (orangeites), and minette lamprophyres [103]

This diverse group of rare rocks are hard to classify; however, all show high concentrations of LREEs (100–2000 rel. to chondrite norm) and even lower than normal concentrations of HREEs (<10 rel. to chondrite norm); and all are the only rocks to be both ultrapotassic (molar K/Na>3) and perpotassic ($Al_2O_3/K_2O<1$). As a group, they tend to lack plagioclase, yet not necessarily be undersaturated, and some are micaceous.

Lamproites are concentrated above extinct subduction zones in continental anorogenic settings, so have likely been enriched by subduction zone fluids.

REEs in granitic pegmatites

The grouping of pegmatities into just a few, or even a single "cohort" of rock types, is something that commonly evokes the scorn of the experts in the field—and the same can be said about carbonatites—nevertheless, we need to start somewhere. Ercit (2005) looking at an earlier classification by Černý noted that although the types included a *rare-earth* type, [104]

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[104] Černý's list has 5 classes, with types and affiliations. These are abyssal class (1 type: none to NYF); muscovite class (1 type: none); muscovite-rare element class (2 un-named types: NYF & LCT); rare-element class (rare-earth type: NYF / beryl type: LCT / complex type: LCT /

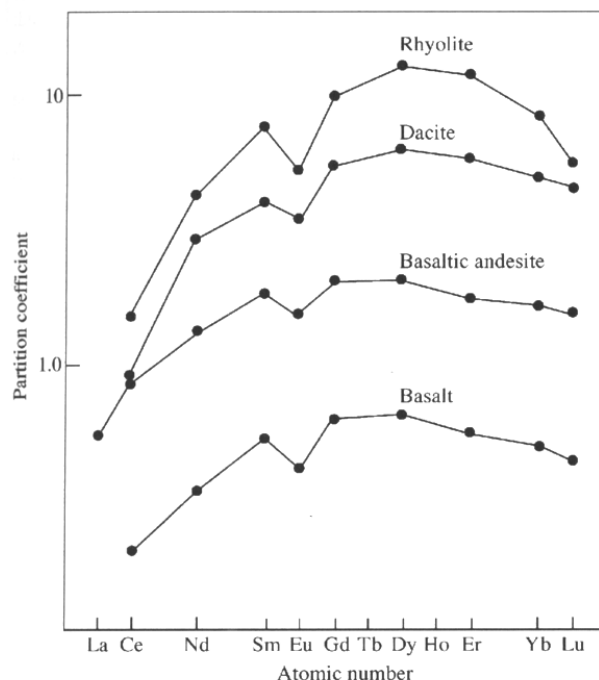[103] Notes in this section are from (Winter, 2010).

Figure 35: Partition coefficients (solid/liquid) of REEs in silicate melts illustrating how fractional crystallization in basaltic magmas leaves REEs in the melt (Kd<1) and how REEs gradually accumulate (Kd>1) in rocks that are more felsic. LCT pegmatites end up being rather low in REEs.   Hollings 2005

REE-enriched granitic pegmatites are also found in several other types. From an REE perspective, pegmatites are therefore (Eric maintains) best thought of as belonging to the:
—LCT (lithium-cesium-tantalum)
—NYF (niobium-yttrium-fluorine), or
—mixed family.

LCTs are peraluminous pegmatites in wet-melt S-type granites and usually contain only low levels of REEs—though counter-examples exist.

NFYs are peralkaline or borderline metaluminous pegmatites in dry-melt A- or I-type granites and are enriched in

REEs—again with a few counter-examples.

Ratios of tantalum to niobium are a good indicator of the degree of fractionation of pegmatites. Tantalum and niobium have almost identical geochemical behaviours and the columbite-tantalite group of minerals comprises solid solutions containing both elements. However, manganocolumbite is less soluble than manganotantalite in silicate melts, and so there is tantalum enrichment in the *residuum*. High ratios of Ta to Nb, as in LCTs are therefore indicative of multiple levels of magmatic fractionation. NYF pegmatites with REEs are *more likely* (there are always exceptions) to have been enriched by a metamorphic process involving melting of an already metasomatic enriched deposit.

Carbonatite rocks

Carbonatite intrusions are far more common than volcanic ones. The REE-rich and ferrocarbonatite (ankeritic) deposits within such intusive complexes are late-stage intrusive dikes of a fine-grained variety called, alvikite.

The main carbonatite-body (usually a coarse-grained variety, calcitic sövite) always has a distinctive aureole typically containing sodium clinopyroxene (aegirine), sodium amphiboles (arfvedonite, glaucophane) , phosphates, iron and titanium oxides, and in some cases K-feldspar. These typical accompanying metosomatic rocks are called "fenites", Figure 36 and 37.

The puzzlingly common "together-but-separate" association of carbonatites with alkaline silicate rocks in REE deposits might be resolved by evidence that alkaline silicate and carbonatites liquids

albite-spodumene type: LCT / albite type: LCT); miarolitic class (2 types: LCT & NYF).
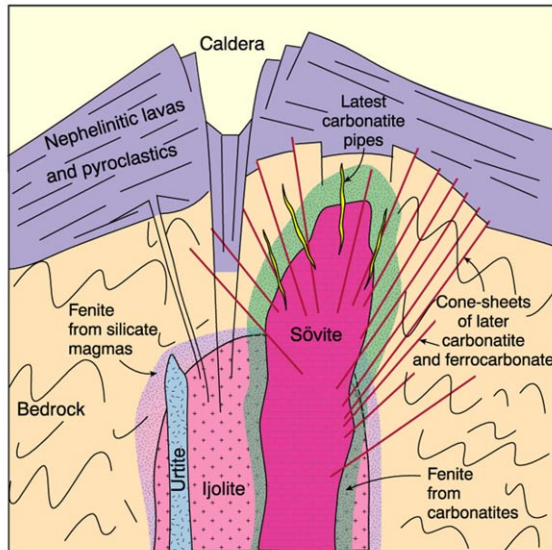
Figure 36: Cross-section of a carbonatite-alkaline silicate complex. Sövite is a variety of carbonatite; ijolite is a nepheline-augite rock; urtite is mainly nepheline. REEs are concentrated in ankeritic alvikite "pipes".

Winter 2010, Fig. 19.11

Figure 37: A carbonatite intrusion in Gujarat, India, within the NW Deccan Trap region. It is 65.5 Ma old, the same age as the flood basalts.   Viladkar 2012
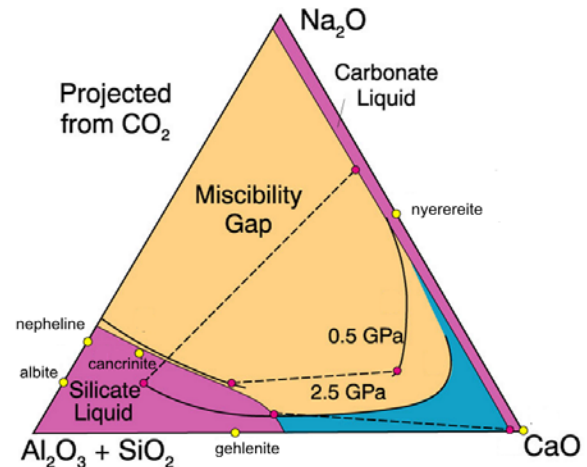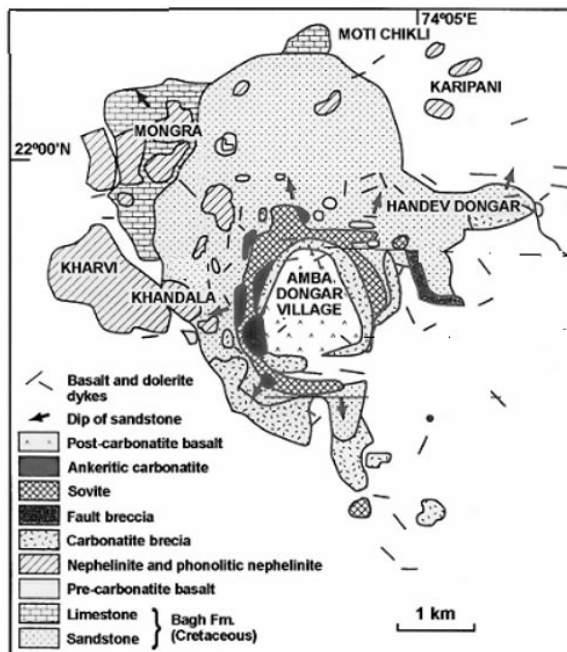
Figure 38: Alkaline silicate–carbonatite liquids in magma saturated in CO_2.

Winter 2010, Fig.19.15

are mostly immiscible, Figure 38.[105] However, whether this applies at high pressure is unresolved.

Some petrologists have also argued that derivation from a parental silicate magma, whether by fractional crystallization or by immiscibility, cannot produce the high levels of REEs, Nb, and incompatible elements characteristic of carbonatites, nor is there enough CO_2 in possible parent magmas to produce the volumes of magma seen in most localities. Whence they come hither thus remains undecided (Jones 2013).

REEs in metamorphic and metasomatic rocks

Classical metamorphism is the in-situ mineralogical change of a rock without appreciable change in its chemistry, and as such, is not a common mechanism for the transportation of REEs. Most of the available data suggests the REE levels and

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[105] Nyerereite is $Na_2Ca(CO_3)_2$; gehlenite is $Ca_2Al[AlSiO_7]$; cancrinite is a carbonate feldspathoid, $Na_6Ca_2[(CO_3)_2|Al_6Si_6O_{24}].2H_2O$; and nepheline is $(Na,K)AlSiO_4$.

patterns are essentially unaffected by metamorphism, with the exception of europium. (Hollings, 2005)

Metasomatism—the chemical alteration of a rock by hydrothermal and other fluids—however is often invoked as an explanation for local concentrations of REEs in major orebodies and occasionally in non-sulphide skarns.

By "fluids", most authors mean aqueous fluids, commonly brines, but away from the surface where pressures and temperatures are much higher, or in the presence of fluxing elements, the dissolved load may become so high that the distinction between a melt and a fluid becomes blurred.[106]

Skarns

Although skarns can be valuable sources of base-metals and gold (Au, Cu, Mo, Sn, W, and Zn-Pb), they are not a common source of REEs—REE sulphides are not stable in damp air—however, localized REE-rich skarns do exist.

The REEs in these skarns are concentrated in specific minerals such as garnet, vesuvianite (idocrase),[107] epidote, and allanite. Vesuvianite and epidote with up to 20% REE have been found in some gold skarns and zinc skarns.[108] REEs are also occasionally associated with sulphide-lean molydenum skarns (and porphyries), which usually contain a variety of metals.

Some unusual skarns contain economic concentrations of REEs together with uranium and its daughter elements.[109] Their geochemistry suggests that these were concentrated in high-temperature hydrothermal fluids.

Iron-oxide copper-gold (Olympic Dam type)

Many diverse ore systems are classified together as iron oxide copper-gold (lOCG) deposits based on an empirical definition arising primarily from geochemical features that do not specify tectonic setting, geologic environment, or sources of ore-forming fluid, metals, or other ore components. Such deposits have abundant magnetite and hematite; hydrothermal ore styles; and no clear spatial associations with igneous intrusions as, for example, displayed by porphyry and skarn ore deposits (Williams 2005).

Most IOCG deposits occur in crustal settings with extensive and commonly pervasive alkali metasomatism, and many are enriched in a distinctive, geochemically diverse suite of minor elements including various combinations of F, P, Co, Ni, As, Mo, Ag, Ba, LREEs, and U. Fluid inclusion evidence suggests that geochemically complex brines, commonly with a carbonic component, were involved in IOCG genesis; however, the ultimate sources of water, CO_2, metals, sulphur, and salinity have yet to be well constrained, and it is possible that these components may have different origins from deposit to deposit. Some IOCG deposits are evaporites with no magmatic involvement (Hunt 2007).

REEs in IOCG deposits (commonly called Olympic Dam type deposits) will always

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[106] At 600"C, silica (quartz) is 5000 times more soluble than at the surface. Alumina (corundum) however remains insoluble. Among cations NaCl solubility>KCl>$CaCl_2$>$MgCl_2$, and common anions are CO_3^{2-}, HCO_3^-, SO_4^{2-}, and Br^-.

[107] Vesuvianite is $Ca_{10}Mg_2Al_4(SiO_4)_5(Si_2O_7)_2(OH)_4$

[108] An excellent reference on skarns is: http://earthsci.org/mineral/mindep/depfile/skarn.htm

[109] An example is the Mary Kathleen skarn deposit in Australia.

be a secondary—which is not to say insignificant—consideration if and when it comes to deciding to exploit them.

REEs in sedimentary rocks and sediments

Almost identical normalized REE concentration figures to those given in Figure 27 for shales have been obtained for terrigenous sedimentary rocks from all over the world.[110]

Typically, with a few exceptions in very arid climates, clays contain higher concentrations than silt, and silt contains higher concentrations than sand.[111] This disparity tends to decrease as one moves from the interior of continents to the coast because large rivers do not transport heavy clay particles very well. However, HREEs appear to mobilize and travel somewhat further than the LREEs in high-energy mountain streams.[112] This accords with the presence of HREEs in concentrates of denser minerals, most notably gold, in placer deposits on alluvial planes.

Placer and paleoplacer deposits

Most placer accumulations with significant amounts of REE minerals are Tertiary or Quaternary deposits derived from source areas that include granitic rocks or high-grade metamorphic rocks; however, some paleoplacer deposits that date back to the Precambrian contain REE resources.

The source for the placer sediments need not be an alkaline igneous rock or a related REE deposit. Many common igneous, metamorphic, and even older sedimentary rocks contain enough monazite to produce

a monazite-bearing placer, and as a result, monazite is almost always found in any placer deposit. However, the types of placers with the greatest concentrations of monazite are typically ilmenite-heavy mineral placers, which have been mined for titanium oxide pigments, and cassiterite placers, which are mined for tin. (USGS 2010)

Many small-scale commercial deposits of REEs are in sands of marine origin along or near present coastlines. The REEs, sometimes the more valuable HREEs, are contained in zircon, monazite, and sometimes xenotime, and are by-products of titanium mineral production.[113]

In the 1980s, monazite and xenotime from titania-zircon paleobeach placers in Australia were the third most important source of REEs in the world, but Australia currently exports little or no REE minerals from such sources, owing to their high thorium content. (Castor 2006)

Laterites (ionic absorption clay)

Lateritic deposits that occur over low-grade primary sources, such as carbonatites and syenites, have been studied as potential REE sources since the 1980s. (Castor 2006) Such deposits may constitute large resources and some have high REE contents; however, only deposits in China have been exploited to date.

REEs have been produced in increasing quantities in recent years from surficial clay deposits in southern China. In 1992, REEs from these deposits comprised 14% of Chinese production and this source has had a strong impact on yttrium supplies since 1988. The deposits reportedly form

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[110] Taylor & McLennan 1988, Fig.39.

[111] Taylor & McLennan 1988, Fig.41. The trend for LREEs and HREEs is the same.

[112] Haskin 1979, p.12 & Fig. 21.3.

[113] The late-Precambrian Athabasca Group near Wheeler River in Alberta contains sandstone with similar characteristics.

weathering crusts over granite. The ore, referred to as REE-bearing ionic absorption clay,[114] mostly comes from two sites—Longnan and Xunwu, the former yielding HREE- and yttrium-rich material and the other, LREE-rich material. Ore from Longnan has an HREE-dominated distribution pattern very similar to that of xenotime, whereas ore from Xunwu is relatively enriched in lanthanum. Both ores have relatively low cerium content, suggesting deposition from oxygen-rich REE-bearing groundwater that has been depleted of cerium as a result of the extreme insolubility of cerium dioxide.

The ore bodies are 3–10m thick and occur mainly in a wholly weathered zone composed of halloysite and kaolinite with residual quartz and feldspar. The deposits are considered to be laterites and show similarities to a number of other lateritic deposits formed over alkaline igneous rocks and carbonatite.

Concluding remark

Note: The composition of an igneous rock is a function of many variables—the concentrations of the elements present (at a minimum Si, Al, Na, K, Fe, Mg, and Ca); the temperature and pressures at which the magma crystallized; the concentration of volatiles (CO_2 and H_2O) in the magma; the extent of partial melting (the selective melting and subsequent transportation of only certain minerals); the extent of fractional crystallization (the selective solidification and immobilization of only certain minerals); the extent of the miscibility of the constituents of the melt; and the degree and type of any metamorphism (particularly hydrothermal metamorphism).

While it is possible to correlate the presence of REEs in a rock—positively or negatively—with (say) other elements or minerals, it remains, at least statistically, impossible to draw conclusions as to the causes of these correlations. Petrologists face a problem similar to that facing those using multivariate analyses as part of an epidemiological or economic study. You can show that under such-and-such a set of circumstances, this-and-that is likely to occur, but you can't prove conclusively why.[115]   ◊

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[114] The cation-exchange-in-clay concentration mechanism was the basis of the zeolite method used in the period 1940–70 for separating REEs in industrial quantities.

[115] An example might help. If mineral A and mineral B often occur together, you cannot say that mineral A occurs *because* mineral B is present; it might be that mineral B only occurs when mineral C is absent, and the real reason mineral A is present is *because* mineral C is absent. One can only present possibilities, not certainties from a statistical analysis made with only a partial set of variables. Petrologists are constantly searching for meaningful subsets of variables—commonly bivariate subsets presented as Harker diagrams—the selection of which will vary from investigation to investigation.

Petrology of the REEs
—with emphasis on continental alkaline magmatism

In this section, I want to focus on the formation of silica-undersaturated rocks and peralkaline rocks, all from the perspective of their geological context and their petrological origin. These types of rocks are the ones most often associated with rare elements, including REEs.

From a geochemical point of view, REEs are dispersed elements, and many processes are involved in their concentration into ores. The first step however is *nearly always*—one has to use absolutes only very cautiously in this subject—their separation by various magmatic processes, such as fractional crystallization, partial melting, and magma mixing, followed by various degrees of metamorphism, including crustal melting, and/or metasomatism. This is a multi-step process, but it begins with the enrichment in REEs of the earth's crust relative to its mantle.

In taking this approach, I will sometimes stray away from treating REEs as a commodity, considering them instead to be an investigative tool. However, this is a part of the evolution of my understanding of REE ores and igneous and metamorphic rocks in general. A more informed and pertinent account will have to wait until later.

The earth's crust

The crust comprises about 1% of the volume of the earth. There are two types, oceanic crust and continental crust.

Oceanic crust is about 10 km thick and has a basaltic composition.

Continental crust is typically about 30–45 km thick below continents, rising to 50–60 km below mountains (orogenic areas),

reaching a maximum in a few localities of 90 km. Continental crust has an overall composition that is roughly granodioritic, but it is very heterogeneous, both in depth and laterally. The amount of continental crust has been increasing with time.

The earth's mantle

The earth's mantle is inaccessible; attempts to drill into it from the earth's surface are years away from completion. It extends from below the crust to 2900 km deep, or 3470 km from the centre of the earth. It comprises about 84% of the earth's volume. Below the mantle is the core. The mantle is composed predominantly of Fe-and Mg-rich silicate minerals.

The mantle is divided by seismic and geochemical discontinuities into an upper mantle and a much larger lower mantle.

Upper mantle

The upper mantle is divided into zones that reflect the complexities of the transition between the lowermost crust and the mantle.

Lithosphere: The uppermost upper mantle is rigid and hard, and together with the crust forms the lithosphere.[116] The lithosphere is that part of the earth's surface that is broken up into tectonic plates.

The thickness of the crusty uppermost upper mantle is variable, ranging from being just a few kilometres below mid-ocean ridges, to about 90 km thick below

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[116] The lithosphere is one of three subdivisions of the earth based on rhenological properties (how materials deform) as opposed to divisions based on composition.

oceanic crust. Below continents, it extends the lithosphere to a maximum of around 220 km deep.

Perisphere: "Perisphere" is not a widely used term—Winter (2005) does not have an entry in his index. It is defined by those that use it, mainly geophysicists, as a thin or in some localities absent, weak layer at the base of the "strong" part of the lithosphere. It is envisaged as being enriched in incompatible elements; being hotter below continents but cooler than the upper mantle, but despite that being more buoyant and less viscous as a result of its chemistry; as having some lateral mobility; and as being isolated from circulating convection cells beneath it.

Asthenosphere: The asthenosphere is the highly viscous, mechanically weak, and ductile-deforming region of the upper mantle. It extends from the lithosphere (including the perisphere if you recognize that concept) down to the boundary with the lower mantle about 670 km deep; though some geologists recognize an important transition zone in the upper mantle between 410 and 670 km.

The asthenosphere is the "lake" on which the tectonic plates "float"—a bad analogy if taken too far because it is a mistake to regard the mantle as being liquid. Practically all of it is solid rock, albeit less rigid rock than in the crust.

Isostatic depression by ice during ice ages is due to lateral movement within the asthenosphere.

Lower mantle

The lower mantle, which appears to be fairly homogeneous (reflecting perhaps our lack of knowledge), starts at about 670 km deep. It may not be chemically very different from the upper mantle, but the minerals in it (olivines and pyroxenes) will

be highly-compacted isomers that are not stable at lower pressures.

The lower mantle is the mesosphere in a lithosphere-asthenosphere-mesosphere sequence.

Mantle-core boundary

Conditions within the 40-km boundary layer of the lower mantle just above the core (the D" layer), 2900 km deep, are the subject of much speculation. There may be liquid there, possibly as a result of radiogenic heating by uranium-238 and thorium-232 in the core; or it could be a remnant area of primordial heat from a time early in the earth's history when much more of the mantle was molten.

The earth's core

The earth's core has a markedly different iron-rich metallic composition from the mantle. Its outer core is in a liquid/molten state. There might be concentrations of REEs in the core, along with other heavy metals, but nobody knows if this is so. Most compositional estimates put the emphasis on siderophile elements rather than lithophiles, although (I note), uranium and thorium are lithophiles, like REEs.

Convection and volcanism

The heat from the earth's interior

The heat flow from the interior of the earth is approximately equally divided between heat left over from when earth first coalesced and radiogenic heat.

The larger portion of the radiogenic heat (presumably) has its source in the core, but it is interesting to note that the decay of potassium-40 accounts for perhaps 20–25% of all radiogenic heat, and this source
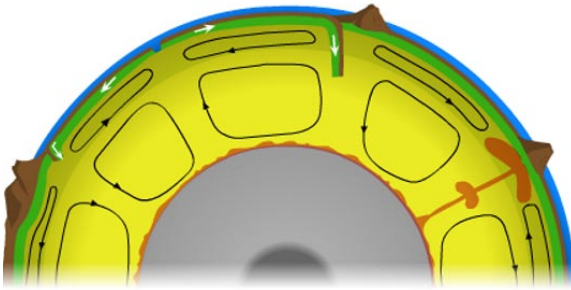
Figure 39: A rare sketch of convection cells in the mantle showing two conjectured shells of cells rather than one generally-accepted whole-mantle shell.

is located within the mantle and crust, not below them.[117]

Convection

The simplest explanation—and hence by Occam's razor rule the most likely explanation—for the structure and composition of the mantle is that heat flows from deep in the earth to the surface by convection. There are hundreds of images posted on the web that liken this convection to the convection that occurs in water in a pot on the stove.

A variant of this model that I rather like—though I had to spend over ten minutes to find a picture of it—shows a degree of separation between convection cells in the upper and lower mantle, Figure 39.

An intramantle shell of convection cells below the crust, above an intramantle inner shell of cells above the core might explain enduring differences in REE distributions within the mantle (which I will come to shortly). This model however I hasten to add is not popular, presumably, in part, because it complicates the standard model without resolving a

commensurate number of problems.[118] Convection patterns within the mantle are also next-to-impossible to observe.

Melting

Melting of rocks to form relatively small pockets of magmas at various depths within the upper mantle are the result mainly of decompression melting and changes in composition.

When the temperature of a rock is raised, the atoms tend to move apart and the rock becomes less dense. But this process is frustrated if along with the temperature rise there us an increase in pressure. Most rock in the mantle thus remains fairly solid, despite being at temperatures where it would readily melt at the surface.

Decompression melting occurs at divergent (pull-part) plate boundaries when the thinning of the lithosphere provides a route to the surface of mantle material that is under a great deal more pressure than exists at the surface. As mantle material rises into lower pressure zones, it expands, which reduces its density, furthering the upward movement, and it melts because it retains its high temperature (in adiabatic conditions).

Hotspot (intraplate) volcanism involves the transfer of heat from close to the mantle-core boundary in pipe-like plumes that traverse (so it is speculated) the whole mantle.

Illustrations of hotspot plumes are plentiful on the web and in textbooks; yet, fully understanding and explaining this process may require a deeper understanding of convection currents

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[117] Perkins S. 2011. *Earth retains much of its original heat*, Science Now, July 17.

[118] There is nevertheless considerable on-going debate among seismologists as to whether or not whole-mantle convection actually exists.

within the core than we currently have.[119] Theories of the instabilities in the lower mantle that lead to the development of plumes have to include allowance for the fact that at extreme pressures, materials become more viscous—although the sinking speeds of subducted lithosphere don't support the idea of large changes within the mantle—their thermal conductivity increases (they cool more readily), and their expansivity (thermal expansion coefficient) decreases which reduces convection at higher temperatures.

One of the noteworthy features of hotspot volcanism is that at the surface, immediately above the axis of the plume, the magma is tholeiitic, but this is surrounded by a halo of more alkaline magma. This halo is seen as a cross-section of the plume head with a hot central area immediately above the vertical axis of the plume, surrounded by cooling magma moving out radially from the centre. This off-axis cooling magma is more alkaline because alkaline magma has a lower melting point than more silica-rich magma and so flows further before becoming too viscous. The same alkaline trend is seen in older volcanoes that are nearing the end of their life.

The plume halo feature neatly accounts for the alkaline→tholeiitic→alkaline trend of Hawaiian volcanoes with age. It is exactly the sequence one would expect as a tectonic plate moves toward, over, and away from, a more-or-less stationary plume.

Another cause of melting is the lowering of the melting point of the rock by volatiles. This is more accurately

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[119] For a thought-provoking account of mantle convection and problems with the current paradigm see Anderson D. 2013. *Mantle Convection*, at http://www.mantleplumes.org/Convection.html.

described as a partial melting process as the resulting magma is a mush of liquid and solids, with the volume of liquid commonly being less than the volume of solids. Subducting tectonic plates at convergent boundaries are loaded with water and carbon dioxide. When they have subducted to a critical depth, these volatiles are driven off by the high temperature, and they subsequently move rapidly upward into the accretion wedge at the top of, and above, the subducting plate. The combination of heat from below and the lowering of melting points by volatiles produces plutonic magma in the wedge.

Some solid-solid phase changes and chemical reactions are exothermic and these may also contribute to localized melting deep within the mantle.

Earth's continental crustal enrichment in REEs

One of the several ways of checking whether or not the perceived enrichment of the earth's continental crust in REEs relative to its mantle and core is real, and not due to a misunderstanding of its primitive, presumed chondritic, composition, is to look to see if the same enrichment has occurred on other terrestrial planets and their larger moons. The news from both the moon and mars, both of which had at one time a molten interior, is good.

Lunar surface

Rock samples brought back from the moon show evidence of fractionation of REEs similar to that seen on earth. If you look at Figure 40 and compare it with Figure 41, you can see, despite significant detailed differences, the range of enrichment, 10-100, compared to the chondrite norm is the same order of magnitude for both.

Most of the samples of basalt brought back by the Apollo missions have a broadly similar flat, but enriched, characteristic.[120]

Two of the samples, known as KREEPs (14310 & 65015; rich in potassium, REEs, and phosphorus) show enrichment greater than 300 compared to the chondrite norm. These have been interpreted as being, in part, the residua of lavas now forming the moon's maria.

The conclusions from many such comparisons are:

—the moon once had a molten core like the earth

—fractionation that is observed in the earth's continental crust, like the moon's, likely occurred early in the history of the solar system; and

—fractionation within the earth's crust, unlike the moon's, is on-going and is a result of processes that differentiate LREEs from HREEs and that are associated with tectonic activities.

Hints of REE and incompatible element depletion in the moon's upper (former) mantle are seen in Sample 67667 obtained from the rim of a large impact crater, Figure 42.

Martian surface

In recent months (Jan. 2013), a meteorite from Mars (Northwest Africa-7034) has provided collaborative evidence, additional to that provided by

Figure 40: REE concentrations in samples retrieved by the Russian probe Luna 16 from the moon's Mare Fecunditatis. The samples are *ca.*3.4 Ga old.

Lunar Sample Compendium, Meyer 2011

photographic studies, that Mars has or had tectonic plates. This evidence relies on the fractionated distribution of REEs, and is shown in Figure 43.
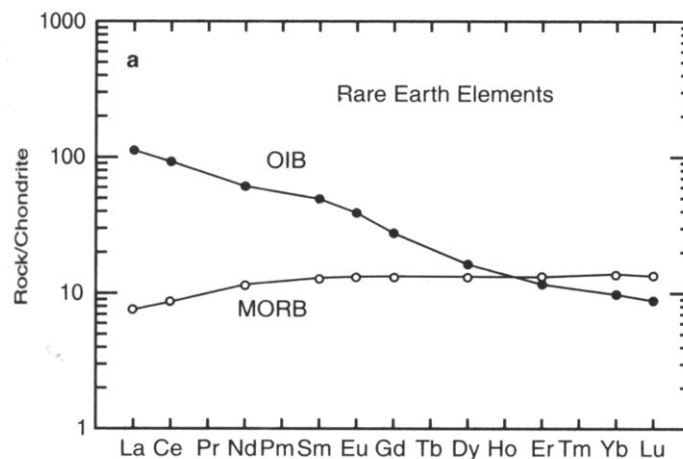
Figure 41: REE concentrations for two types of terrestrial basalt. MORB = tholeiitic mid-ocean ridge basalt (N-type); OIB = alkaline ocean island basalt (OIA-type). See text for additional notes.

Sun & McDonough 1989

[120] Except that is for a strong negative anomaly for europium that is matched by a strong positive anomaly in the abundant lunar anorthosite. The anomaly, due to incorporation of Eu^{2+} in calcium feldspar, is not seen on the earth's surface because europium is readily oxidized to Eu^{3+}.
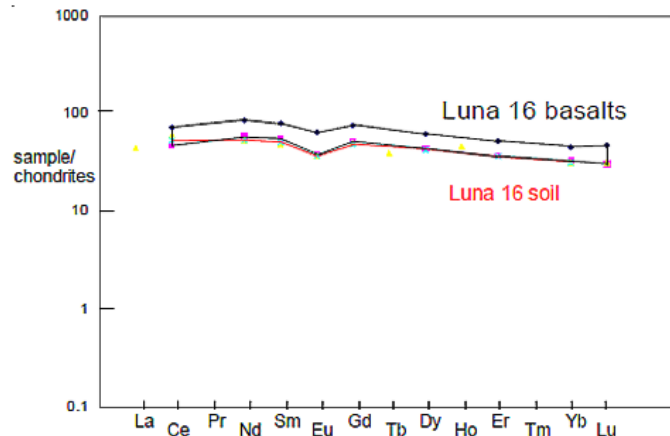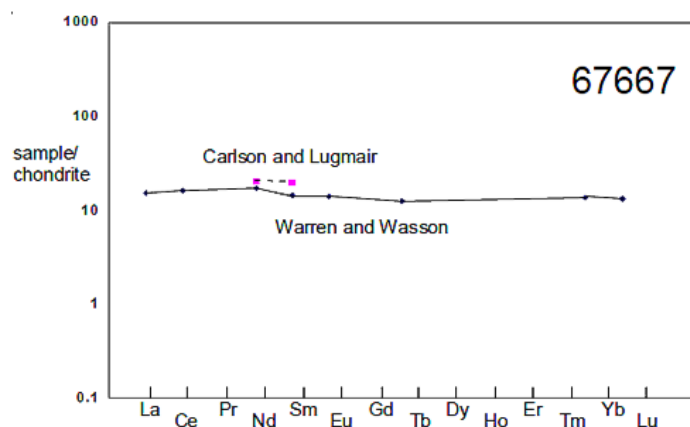
Figure 42: REE concentrations in an unusual feldspathic lherzolite from the rim of the North Ray Crater retrieved by Apollo 17. It is 4.2 Ga old. Note the lack of LREE:HREE fractionation, a feature of most lunar samples, and the relatively low levels of REE enrichment.

Lunar Sample Compendium, Meyer 2011

Ocean island alkaline basalt (OIA-type OIB) is a characteristic intraplate hot-spot magma, and is enriched in LREEs and other incompatible elements from a deep mantle source likely similar to that of the E-type MORB magmas (Winter, 2010d).

Alkali basalts can also be the result of fractionation at shallow depths. There is also a more common, less alkaline (tholeiitic), basalt (OIT-type OIB) that is not so LREE enriched as the OIA-type. Tholeiitic basalts are likely from shallower, wetter, more partially-melted sources than the OIA-type, but again fractionation, this time at depth, may also play a role.

REEs in the asthenosphere

Looking again at Figure 41, since there is no known process for enriching a residual melt with HREEs (thanks to lanthanide contraction, HREEs are more, not less, compatible than are LREEs), N-type MORB magma (mid-ocean ridge) like the one shown here must have been at least partially derived from a source already relatively depleted in LREEs and other incompatible elements. The current supposition is that this source is the upper mantle, and that its depletion mirrors enrichment of the crust (Winter, 2010c).

There are also E-type MORB magmas that do not show relative LREE depletion, and the source for these may in the lower mantle, perhaps even down to the core-mantle boundary, where crustal material has been reintroduced by subduction.

REEs in continental settings

There are two circumstances where volcanism occurs on continents: hotspot volcanism and continental rifting, which
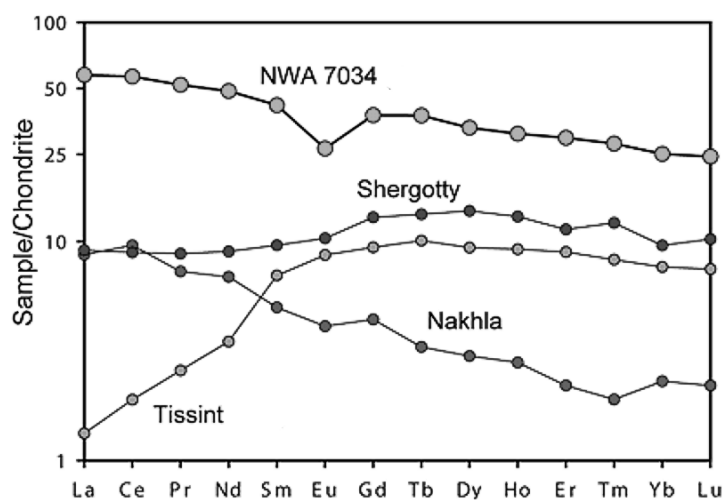

Figure 43: REE concentrations in four meteorites from Mars showing variable LREE:HREE fractionation like that seen on earth, but not on the moon. NWA 7034 is 2.1 Ga old and contains plagioclase,K-feldspar, ilmenite,and apatite.   From Agee et al. 2013.

Sciencexpress doi: 1126/science 1228858

includes extension as a result of failed rifting.

Continental hotspot volcanism is basaltic and as such has not aroused any interest in the search for REEs. However, undersaturated peralkaline and carbonatite rocks, which most definitely have, typically occur in areas of continental rifting. This is in sharp contrast with their general lack of occurrence in oceanic rift zones (MORBs). Peralkaline rocks are not completely unknown on oceanic islands, but they are rare and usually then only mildly peralkaline.

Flood basalts

Flood basalts are an interesting phenomenon and worth a slight diversion. The most well known flood-basaltic areas are the Deccan and Siberian Traps, but the Karmutsen Formation on Vancouver Island will also be a familiar example. Regardless of whether it is true or not, my favorite explanation for flood basalts is that they occur when a continental rift or extension coincides with a hotspot.[121]

Flood basalts are not repositories of REEs, but their distribution in trace amounts in the basalt nicely illustrates the value of using REEs as "fingerprinting" agents.

Figure 44: The evolution of REE distributions in Wrangellian flood basalts LREE-depleted to LREE-enriched, together with isotopic data, helps track the evolution and petrogenesis of the formation

Greene et al. 2008

Greene et al. (2008) suggest (I'm simplifying possibly to the point of distortion) that the Wrangellian eruptions started with a basaltic magma that contained a significant pre-existing lithic component introduced by thermal and mechanical erosion by the impinging plume head. This initial magma flow was LREE-depleted, low-Ti, with pronounced HFSE anomalies, and an REE distribution, shown in the upper diagram of Figure 44,

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[121] An also-ran theories is that they result from a rythmic release of magma from a particularly large chamber where they had been gradually accumulating and confined for a long time. Some argue that they are a result of lithospheric thinning by extension in a failed rift alone.
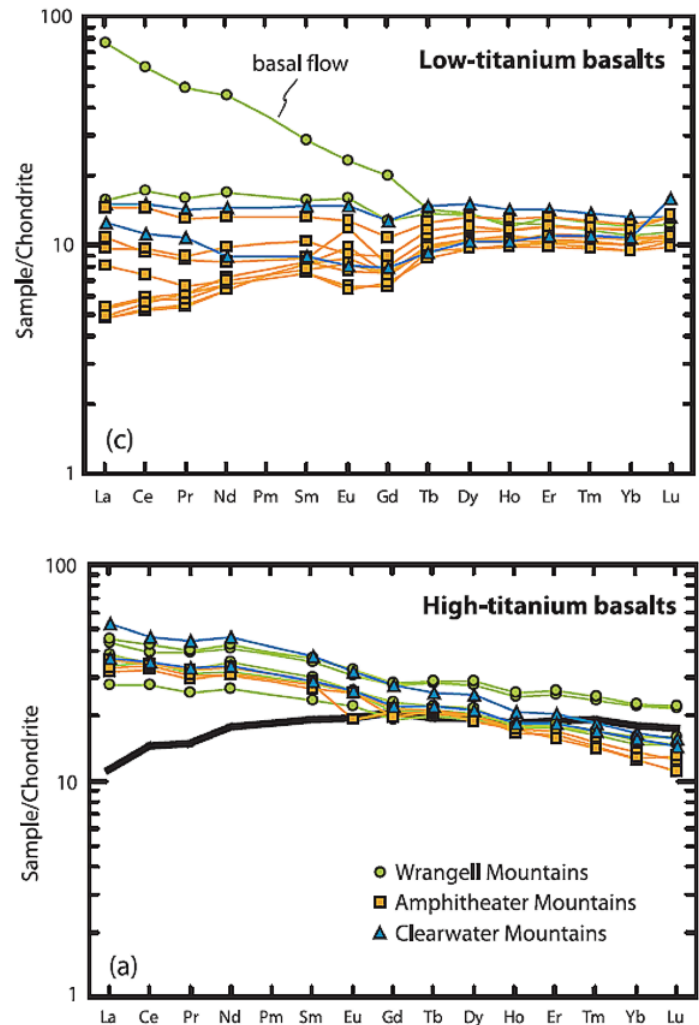
not too different from that of OIB magma (OIT-type, not the OIA-type in Figure 41).

At a later stage in the prolonged eruption of the flood basalts, the magma became more LREE-enriched and high-Ti, shown in the lower diagram of Figure 44, corresponding to E-MORB magma (E-type, not the N-type in Figure 41).

This change over time from LREE-depleted to LREE-enriched, Greene et al. suggest was as a result of the later magma from the lower mantle becoming less "contaminated" with shallow-source characteristics as the magma cleared pathways through the crust.

Continental rifts

Peralkaline, alkaline, and carbonatite rocks that contain concentrations of REEs are almost universally found in rocks associated with both ancient and modern continental rift zones, Figure 45. Crucial to the development of ideas on the petrogenesis of REE ores is thus an understanding of mantle convection stratification below cratons. Unfortunately, information as to what goes on below thick continental crust is harder to come by than in oceanic settings.

Tomographic 3-D views of the mantle obtained from seismic records do not always correlate well with views deduced from geochemical data. This may well be just a result of a failure of geochemical boundaries to provide strong shear-strength and -velocity anomalies; and conversely, strong shear-strength and -velocity anomalies are not necessarily indicative of significant geochemical boundaries and barriers.
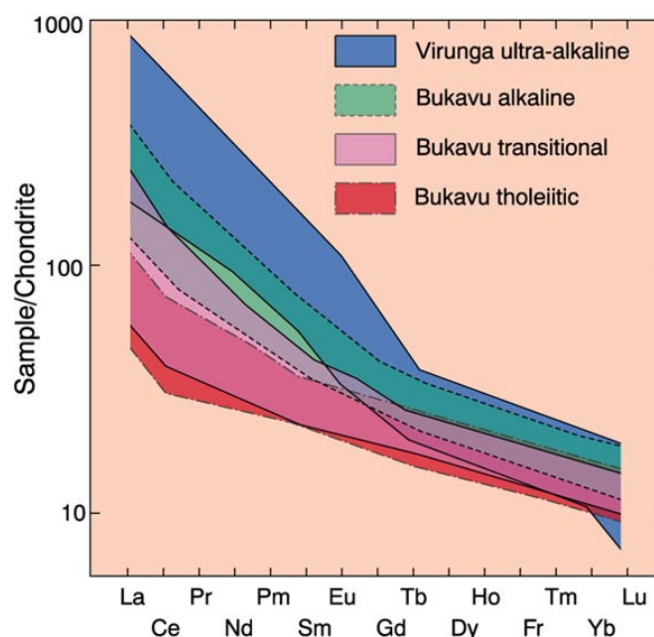
Figure 45: High LREE enrichment is found in deposits associated with alkaline and peralkaline rocks in regions of continental rifting, in this case the East African Rift.
Winter 2010, Fig.19.5)

The prominent seismic discontinuity at 670-km depth, for example, is widely interpreted as an endothermic phase change boundary. Although this may alter the sinking velocity of cooling subducted slabs, it is not sufficient to prevent slabs from passing right through the boundary and cascading down into the lower mantle.

Figure 46 shows a spherical-harmonic analysis of shear-wave propagation through the mantle.

Note: The mathematics of seismic spherical-harmonic analysis is identical to that used in quantum-mechanics to characterize the spatial distribution of electron wave functions around atoms (see Figure 9). While you can extract some information from a time-varying pressure waveform, say, of a note played by a musical instrument, the information is not complete without an examination of its (Fourier) harmonic spectrum. In the same way, it is helpful to understand seismic

shear-wave data by examining the (Laplace) spherical harmonic spectrum.

In the frequency domain, you can easily pick out significant spectral differences between, say, an oboe and a violin playing the same note. In the spherical harmonic domain, you can easily spot differences in the distribution of shear-wave propagation from low frequencies (wavelengths and distances spanning the entire globe) to short frequencies (small intracontinental and oceanic basin wavelengths and distances).

In the diagram, Figure 46, changes of colour along a vertical axis for any degree of harmonic indicates stratification. Changes in colour along a horizontal axis indicate some degree of lateral heterogeneity. Varying rates of transition between red and green on a horizontal axis indicate varying degrees of heterogeneity. If shear-wave attenuation, at any particular depth, varies significantly and often from location to location, the transition will be gradual—the mantle at this depth is very heterogeneous. And conversely, if the shear-wave attenuation, at any particular depth, is global, then the transition will be sharper—the mantle at this depth is fairly homogeneous. The blue on the right simply indicates that variations over relatively short distances have not been observed, or are essentially random on this distance scale.

What Figure 46 appears to indicate therefore is that the mantle below 670 km down to near the bottom of the lower mantle is fairly homogeneous.[122]

Figure 46: A spherical-harmonic analysis of shear-wave propagation through the mantle. The Y-axis is the power of the shear-wave harmonic (its attenuation with red being least attenuated), and the X-axis is the spherical hamonic degree. Liquids do not propagate S-waves. See text for a fuller explanation of the diagram.   Gu et al. 2001

At the bottom of the mantle near the core, there appear to be low frequency (long wavelength) anomalies, but interpretations of this observation vary widely. Spatial correlation of these anomalies with hotspots is poor. Gu et al. (2001) suggest that the strong degree-2 and 3 signatures below 1800 m might be due to the presence of debris from a few large, still-cool, subduction slabs.

At the top of the mantle near the crust, there appear to be significant high frequency (short wavelength) anomalies. Above 100 m these are created by variations in crustal thickness and possibly by the presence of partial melts. The differences between the degree 5-7-9 set and the degree 4-6-8 set probably reflect the distribution of shields or cratons, but again interpretations vary.

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[122] Either that, or significant boundaries do not show up in the sesimic record. A postulated boundary at 1000 km due to an exothermic phase change of olivine was found not to be required in the data of Gu et al. (2001).

Beside the attenuation of S-waves, seismologists can, using spherical-harmonics to measure phase differences, and hence travel times, and hence S-wave velocities.[123]

S-waves propagate by lateral motion and only through solids—the mantle is mostly in a viscoelastic state and exhibits time-varying elasticity (anelasticity). S-wave velocity decreases with density, but increases with shear modulus (stress/strain; loosely solid-state viscosity). Temperature is a key parameter below the solidus because high temperatures reduce shear modulus, and hence decrease velocity. Composition has relatively little effect.

Figure 47 shows a few results of shear-wave propagation through the mantle—red indicates relatively slow and blue relatively fast. At 100 km deep, the difference between propagation below continents is strongly differentiated from that below oceans. These differences are almost as strong, but different for oceanic areas at 300 km. At 900 km, the mantle has become more homogeneous.[124]

As can be seen in Figure 47, S-wave propagation below continents tends to be somewhat faster than below oceans at
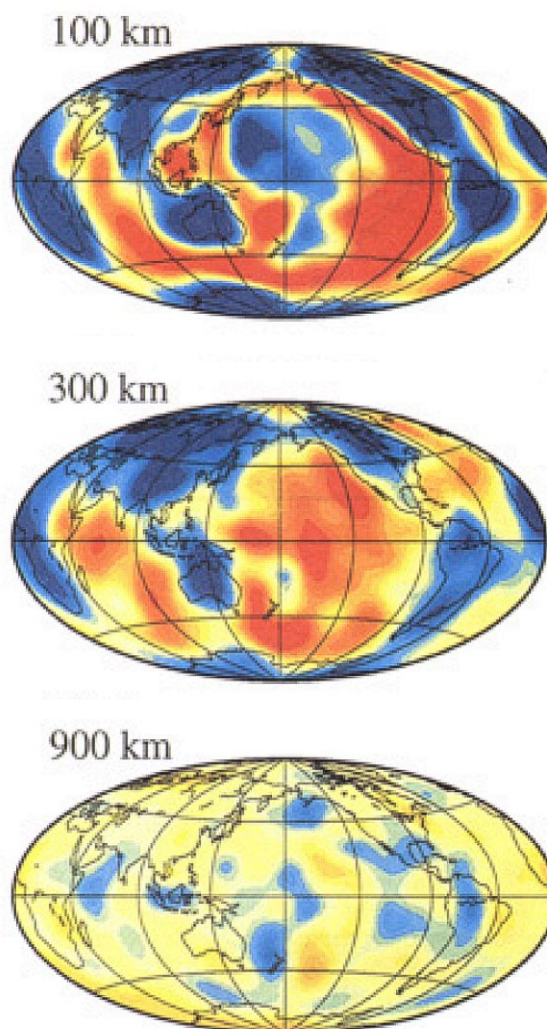
Figure 47: S-wave propagation through the mantle. This view is centred on the Pacific basin. Red areas indicate slower than average velocities; yellow areas average velocities; and blue areas faster than average velocities. See text for a fuller explanation of the diagram.

Gu et al. 2001

300 km, which is consistent with the idea that the mantle there is cooler.[125]

[123] Shear waves propogate by lateral motion and can only be transmitted through solids. S-wave velocity decreases with density, but increases with shear modulus (stress/strain, a solid-state version of viscosity). Since the shear velocity of rocks generally increases with depth, shear modulus must also increase with depth.

[124] The diagrams are deserving of much more attention than given here, but are already sufficiently off the REE topic. The point is that it is too easy to make simplifications about the mantle below continents.

[125] A figure I have seen is 400°C below an average mantle adiabat at 100 km under the Russian Platform (Goes, 2000).

The essence of the relationships between continental rifts and alkaline magmatism is thus that:

—only alkaline magmas have melting temperatures as low as 500 to 400°C and so may, in some circumstances, be the only melts exisiting beneath continents

—beneath continents, sodium, gases, and other volatile elements have no escape route to the surface

—continental lithosphere is stable and old, and so no matter how slowly rare elements and REEs accumulate, they have time to concentrate in quantity

—residua melts at the top of the asthenosphere containing rare and incompatible elements including REEs may form pegmatic-like intrusions into the lithosphere (my conjecture)

—fractures are not normally present at depth because of lithostatic pressure, but when the crust is being extended and faulted as in rifts, perhaps microfractures and micro-veins do occur at depth (my conjecture). If they do, the exceptional volatility and low temperature of alkaline magmas would allow them to physically fractionate by intruding further upward than tholeiitic magmas

—during the late stages of crystallization, sodium-rich fluids can cause late- and post-magmatic alteration and the formation of hydrothermal mineralizations. ◊
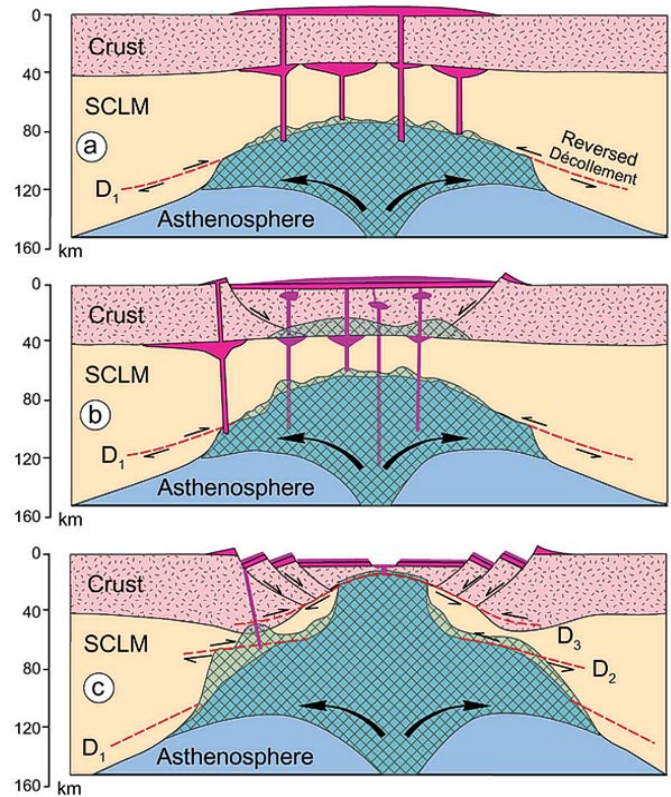
Figure 48: A model of the development of a continental rift.

(a): a superplume in the asthenosphere rises, decompression melting occurs as does partial melting of metasomatized subcontinental lithospheric mantle (SCLM). Localized delamination of the lithosphere (not shown in this diagram) may contribute to thinning of the lithosphere and to recycling of enriched continental underplate to the mantle;

(b): eruption of alkaline and peralkaline magmas. Crust responds to tensile stress by faulting (normal at the surface, décollements D within the mantle) creating a graben;

(c): the asthenosphere ascent nears the surface and basaltic magma (possibly flood basalt) erupts. A rift valley forms. The development begins to resemble oceanic rifting.

Winter 2010, Fig. 19.9

REE ores

Global economic deposits

Global economic deposits fall into one of three classes. Ores that are potentially exploitable; ores that are being exploited; and ores that have been exploited in the past, but are now closed down for economic, environmental, or social reasons. Figure 49 shows the location of some important REE economic deposits, but like all such maps, it could easily be rendered out-of-date by tomorrow's news.[126] The following is a brief, less-than-comprehensive summary of the world's REE resources. A short list of significant sites (those with recent production of REEs underlined) is:

Australia:	Eneabba, Mt. Weld, Nolans Bore, Dubbo, Hastings,
Brazil:	Buena Norte, Araxá
Canada:	Eco Ridge, Hoidas Lake Nechalacho, Strange Lake Kipawa, Eldor
China:	Bayan Obo (Baiyun'ebo), Weishan, Maoniuping, Xunwu/Longnan, Sichuan, South China
Estonia:	Sillamäe
Greenland:	Kvanefjeld, Sarfartoq
India:	Chavara, Heavy-mineral sands
Kenya:	Mrima Hill
Kyrgyzsytan:	Kutessay II, Aktyus
Malawi:	Kangankunde
Malaysia:	Ipoh
Russia:	Lovozero
S. Africa:	Zandkopsdrift Steenkamskraal
Sweden:	Norra Kärr
USA:	Mountain Pass, Bokan Mountain, Bear Lodge
Vietnam:	Lai Châu

Current forecasts for the next few years is that there will be a global production surplus of LREEs (lanthanum and cerium); while demand for HREEs (neodymium,

europium, terbium, dysprosium, and erbium) will be in supply deficit.[127]

Bayan Obo in Inner Mongolia, PR China

China's main REE production takes place in Inner Mongolia and accounted for 50–60 percent of China's total rare-earth concentrate output during the past decade. Sichuan Province was the second leading REE concentrate producer, accounting for 24–30 percent of production (USGS 2011).

The Bayan Obo deposit is the world's largest REE resource and is also exploited as a major iron oxide deposit. Its genesis has been the subject of much debate for many years. The orebody is carbonatite-related with multiple episodes of hydrothermal modification.[128]

The ores show enrichment (rel. to chondrite) is 10^5–10^6 for LREEs and 10^3 for the HREEs,[129] mostly contained in bastnäsite and monazite, minerals that are common sources of REEs but rarely occur together. The thorium content of the ores is low, which makes it easier to process.

> Figure 49 (*next page*): Some global REE deposits. It's hard to find maps from different sources that match, an indication perhaps of how rapidly exploration and development is proceeding. Note the similarity in the nature of the deposits in Russia, Greenland, and eastern Canada. Rifting of Pangea?
>
> British Geological Society: Global REE Deposits 2011

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[126] Chen, Zhanheng, 2011. Global rare earth resources and scenarios of future rare earth industry, Journal of Rare Earths, **29**, 1, pp1–6.

[127] Great Western Minerals Group website, Dec. 2012.

[128] The best description of the Bayan Obo orebody I have found is (Chao 1997); however, be aware that accounts of the origin of the host rock (H8 dolomite marble) in the USGS Bulletin (1997) are no longer up-to-date. (Yang 2011).

[129] Smith 2000, p.3152.

REE
mines

Other REE deposits/
occurences

Carbonatite-associated

Alkaline igneous rock-associated

Iron-REE deposits

Hydrothermal deposits exclusive
alkaline settings

Primary deposits

Marine placers

Alluvial placers

Paleoplacers

Lateritic deposits

Ion-adsorption clays

Secondary deposits

1   Mountain Pass, USA
2   Pajarito Mountain, USA
3   Gallinas Mountains, USA
4   Iron Hill, USA
5   Bald Mountain, USA
6   Bear Lodge, USA
7   Pea Ridge, USA
8   Green Cove Springs, USA
9   Carolina placers, USA
10 Lemhi Pass, USA
11 Snowbird, USA
12 Rock Canyon Creek, Canada
13 Hoidas Lake, Canada
14 Thor Lake, Canada
15 Elliot Lake, Canada
16 Strange Lake, Canada
17 Ilimaussaq complex, Greenland
18 Araxa, Brazil

19 Barro do Itapirapua, Brazil
20 Lovozero and Khibina complexes, Russia
21 Tamazeght complex, Morocco
22 Bou Naga, Mauritania
23 Nile Delta and Rosetta, Egypt
24 Etanero, Namibia
25 Okorusu, Namibia
26 Steenkampskraal, South Africa
27 Zandkopsdrift, South Africa
28 Plinesberg Complex, South Africa
29 Naboomspruit, South Africa
30 Palabora, South Africa
31 Richards Bay, South Africa
32 Kangankunde, Malawi
33 Congolone, Mozambique
34 Karonge, Burundi
35 Chavara, India
36 Amba Dongar, India

37 Orrisa, India
38 Perak, Malaysis
39 Maoniuping/Dalucao, China
40 Bayan Obo, China
41 Weishan, China,
42 Xunwu/Longnan, China
43 Dong Pao, Vietnam
44 Eneabba, Australia
45 Jangardup, Australia
46 Mount Weld, Australia
47 Brockman, Australia
48 Nolans Bore, Australia
49 Mary Kathleen, Australia
50 Olympic Dam, Australia
51 WIM 150, Australia
52 Dubbo Zirconia, Australia
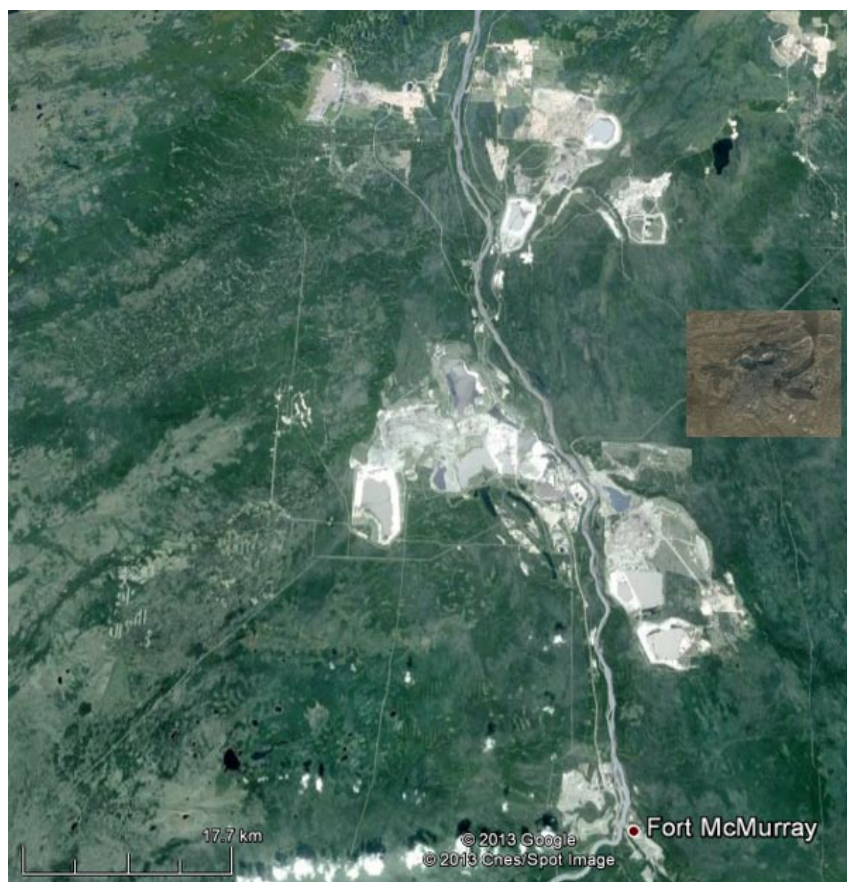53 Fraser Island, Australia

Figure 50: *Left*: The Athabasca oilsands project at Mildred Lake, north of Fort McMurray, Alberta. The inset, on the same scale, and the enlarged picture on the *right* is of Bayan Obo, Inner Mongolia, China where ≈ 48% of the world's supply of REEs are mined.

Compiled by the author using Google Earth.

Mountain Pass in the USA

The Mountain Pass deposit is in a 1.4 Ga old carbonatite intruded into gneiss, and contains 8–12% rare earth oxides, mostly contained in bastnäsite. Gangue minerals include calcite, barite, and dolomite. It is regarded as a world-class rare-earth mineral deposit. The metals that can be extracted from it include: cerium, lanthanum, neodymium, and europium.

Kvanefjeld in Greenland

The current second largest REE deposit in the world, the Ilimaussaq intrusive complex on the southwest coast of Greenland, is a large alkalic layered intrusion containing peralkaline nepheline syenites and a variety of highly-unusual minerals.

Mt. Weld in Australia

Until 1995, Australia was a major producer of REO from monazite, a by-product of heavy mineral sand mining for ilmenite, rutile, and zircon. Although there is no current production of REEs in Australia, REE-rich ore continues to be mined and stockpiled at Mount Weld. The REEs are contained in secondary phosphates and aluminophosphates, presumably derived from weathering of the Proterozoic carbonatite

In other projects, the Nolans Bore REE-phosphate deposit in the Northern Territory and the Dubbo Zirconia Project at Toongi NSW, which is an alkaline trachyte deposit, are undergoing feasibility studies.

Elevated concentrations of REEs have been documented in Australia in various heavy-mineral sand deposits, carbonatite intrusions, peralkaline igneous rocks, iron-oxide breccia complexes, calc-silicate rocks (skarns), fluorapatite veins, pegmatites, phosphorites, fluviatile sandstones, unconformity-related uranium deposits, and lignites.

Reports of mineral resources in Australia routinely include somewhat rueful comments that many valuable resources are "unavailable" because they contain traces of radioactive thorium, or are in the National Park system.

Araxá in Brazil

Announcements of the discovery of large deposits of REEs (carbonatite laterites), especially HREEs, in Brazil are a frequent occurrence these days, but most current production is as a by-product of mining for phosphate and niobium.

Chavara in India

REE production in India is from small scale operations. Two larger companies work placer beach sand deposits containing heavy metals in Kerala.

Sillamäe in Estonia

The uranium mines at Sillamäe ceased production in 1989, but it was subsequently discovered that the tailings contained significant amounts of rare metals including REEs. It now produces niobium, tantalum, and some REEs, and there are plans to expand its current REE production, but the environmental problems created by the former uranium mining are formidable. The deposit is marine black shale,[130] an interesting example of a rare-metal ore produced in part by biological means involving phosphates (Swanson 1961).

Kangankunde in Malawi

The Kangankunde carbonatite complex in Malawi is rich in REE mineralization. It consists of ferroan dolomite and ankerite

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[130] There are such shales in the US (Chattanooga in the NE, Kansas, and Oklahoma) but interest in them these days is mainly for natural gas.
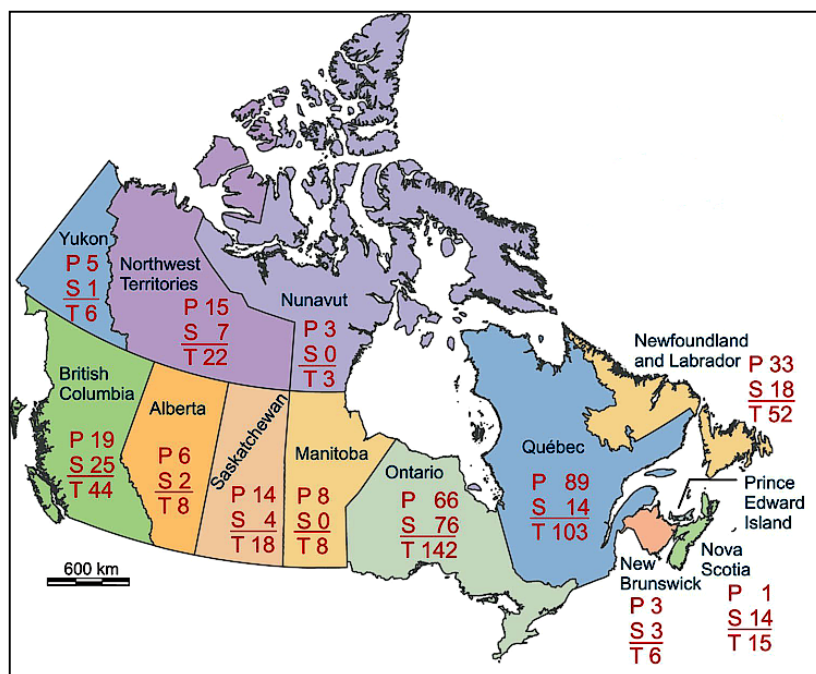
Figure 51: Lanthanide deposits in Canada. P=primary;
S=secondary (a by-product).   Simandl 2012

The only other areas with similar geology and mineralogy are Khibiny Massif (immediately west of Lovozero), Ilimaussaq in SW Greenland, and Mont-Saint-Hilaire in Québec.

Ores in Canada

A heavy lanthanide concentrate (mostly yttrium) used to be produced in Canada as a by-product of uranium processing, but many plants producing uranium and throrium are now inactive.

Hoidas Lake, Saskatchewan

The mineralogy of the substantial REE deposit at Hoidas Lake in Saskatchewan, not far from Uranium City, differs from most other such deposits in that it is hosted in veins of apatite and allanite, a sorosilicate that occurs in metamorphosed clay sediments and felsic rocks. The deposit contains a number of HREEs, such as dysprosium. The mineralization is presumed to be hydrothermal, from a carbonatitic or alkali source at depth, but the two hosts are a monzogranite (a biotite-rich granite) and a granodioritic to tonalitic gneiss.

Strange Lake, Québec and Labrador

The host rock at Strange Lake is a series of HFSE-enriched peralkaline granites, one of which contains numerous pegmatites. The basement rock is quartz monzonite.

The REEs present in the deposit are primarily found in silicate minerals such as allanite, zircon, and gittinsite.[132] There

carbonatites,[131] including some manganese-rich varieties, surrounded by an aureole of inner potassic and outer sodi-potassic fenites. There are no major associated silicate rocks and no calcic carbonatites.

Lovozero in Russia

The Lovozero Massif is underlain by a complex of agpaitic to hyperagpaitic (peralkaline undersaturated) rocks, typically nepheline syenite and phonolite, containing minerals such as eudialyte, loparite (an ore of niobium and tantalum that contains cerium), and natrosilite (anhydrous sodium silicate). At least 105 valid minerals have been described in the massif and 39 minerals were initially discovered there.

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[131] Ankerite is Ca(Fe,Mg,Mn)(CO3)2. "Ferroan" is IUGS-recommended terminology for Fe2+ (ferrous ion); "ferrian" is the Fe3+ (ferric ion) equivalent.

[132] Gittinsite is $CaZrSi_2O_7$.

are also a few phosphate minerals present.[133]

The deposits are of major interest of their unusually very-high (20% of total) HREE content. Some samples have concentrations of 10^4 ppm compared to the chondrite norm (Kerr 2012).

A preliminary model for the evolution of the pluton calls for the injection of a mantle-derived halogen-rich trachytic fluid into a crustal magma chamber. Protracted in-situ fractionation then produced an extremely evolved roof zone from which batches of magma were extracted and intruded to form a high-level pluton. (Salvi 2005a,b) (QRM 2013).

Ores in British Columbia

Although there are several REE deposits in BC, none is close to being developed as a source of REEs alone, rather the focus of the BC Ministry of Forests, Mines, and Lands is on looking at REEs as a potential by-product of operations aimed at extracting other rare metals (RMs), or "specialty metals" as they are often called, principally niobium (41) and its 3rd-transition-series counterpart tantalum (73).[134] [135]

Figure 52: Diamond-drill granite core from the Strange Lake B zone. The deposit is unusually rich in rare HREEs.

Technology Metals Research (TRM), October, 2011.

Of the 108 RM deposits on BC ministry files, nineteen contain REEs (Simandl, 2012a),[136] The RM ore types in BC break-down to, with REEs excluding scandium in parentheses:

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[133] G. Hatch. Technology Metals Research, March 23, 2013.

[134] Less so, but also, their neighbours in the Periodic Table zirconium (40) and hafnium (72). Also classified as RMs of interest are beryllium (4) and lithium (3). A few other RMs have not been selected for close attention. These are niobium's 1st-transition-series counterpart vanadium (23), gallium (31), and germanium (32). See Ministry Information Circular IC2011-2, Targeted Geoscience Initiative TGI-4, and Geofile 2011-10. More common metals associated with RMs in BC

are copper, molybdenum, tungsten, zinc, gold, silver, uranium, and thorium.

[135] Whiteley 2012.

[136] Of the 108, 1 is a producing Mo-Cu-Zn mine (Endako at Fraser Lake); 17 have been developed to the stage where estimates of ore quantity are possible; 15 are deemed prospects worthy of further investigation; 68 are no-drilling showings; and 7 are mines out-of-production, mainly gold mines with one or two silver and beryllium gemstone mines.

42 (4) pegmatite granites with 1 (0)
peralkaline intrusive;
25 (10) carbonatite/syenite;
12 (1) placer/paleoplacer;
7 (6) sedimentary phosphates;
9 (0) skarn; and
13 (3) "others", many of which contain a
range of rare and precious metals.

Although pegmatite granites are the most
numerous RM ore-types in BC—they
frequently contain beryllium—unless other
non-REE metals are involved, the trend is
to prefer minerals that are easily broken
down, such as the carbonatites, rather than
silicates that are difficult to dissociate.

Placer deposits may be problematic
because, if they contain REEs, they likely
also contain thorium, and in BC, it is not
possible to get a mineral licence for the
exploration and development of
radioactive deposits.[137]

There are no recorded deposits of REEs on
Vancouver Island, Haida Gwaii, or the
adjacent mainland; nearly all sites are in,
or near, the Rocky Mountain Trench in the
east of the province. ◊

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[137] Mineral Tenure Act, *Uranium and Thorium
Reserve*, Regulation 82-2008.
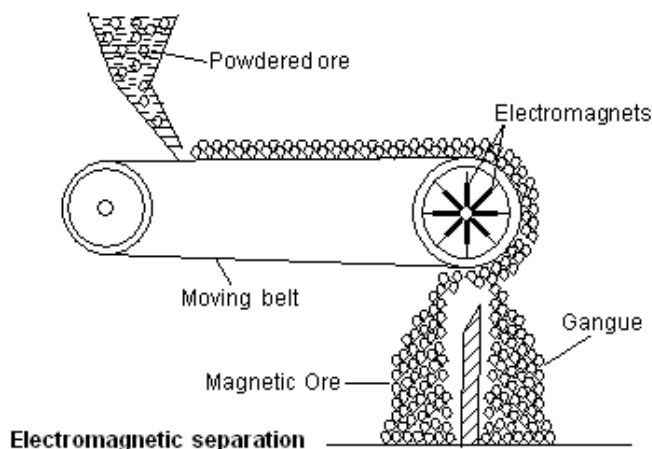
REE extraction techniques

Processing ores

Separating individual REEs from an ore is a difficult and expensive task, often requiring dozens of procedures. This is especially true of the more valuable HREEs.

Milling [138]

The REE ore is first crushed to gravel, and then progressively ground into a fine powder. The powder is sifted and sorted to extract usable material, and the tailings are set aside.

Milling is usually carried at, or near, the mine site, and tailings are dumped in a near-by storage area. These areas are, ideally, carefully constructed to prevent the tailings being leached or otherwise escaping into the environment.[139]

electromagnetic separation, flotation, and gravity concentration.

Electromagnetic separation is used for the most commercially common REE ores, monazite and bastnäsite. However, if the ore is not sufficiently magnetic, or is mixed with substantial amounts of other magnetic material, flotation separation is used instead. This is sometimes the case with bastnäsite.

The flotation procedure is to add liquids to the finely crushed ore in flotation tanks. Chemicals are added to cause some of the impurities to settle out, and air is pumped in to create air bubbles. The finer particles stick to the bubbles, which rise to the top and form a froth that is then skimmed off.

Falcon Concentrator

Concentrating

The next step is to reduce the powder to a concentrate. There are several methods in use for this, the principal ones being

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[138] Most of the information and illustrations in this section are from a brochure published by the Kidela Capital Group. Available Feb. 2013 from: http://www.kitco.com/ind/Kidela/may102011.html

[139] Some REE ores contain radioactive thorium.

Another separation method that can be used exploits the high density of REE ores, and is the same as that used in the gold industry. Centrifuges, called Falcon Concentrators, contain rotating cones or bowls that are spun at high speed.

Compared to other technologies, gravity concentration (so-called)[140] is cheap. It also has less environmental impact because it does not require the use of chemicals.

Separation

The milling process, whichever it is, produces mineral concentrates that contain a substantially higher proportion of REEs than the original ore, but there remains much to be done to separate the concentrate into its constituent REEs.
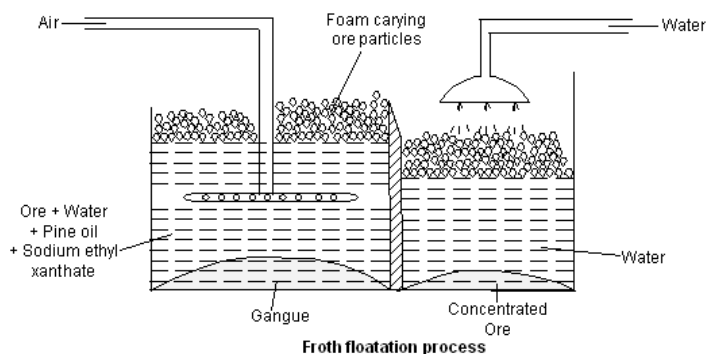
The first step of the separation process is to produce a liquid concentrate. The REE metal or one of its pure compounds, commonly an oxide, is then precipitated from the solution by chemical or electrolytic means.

There are a variety of hydrometallurgical techniques for producing a liquid concentrate. Although hydrometallurgy originated in the 16th century, its principal development took place in the 20th century. The development of ion exchange, solvent extraction, and other processes now permits more than 70 metallic elements to be produced by hydrometallurgy, including the REEs.

Fractional crystallization

Fractional crystallization was the method used by the early chemists and is based on

Froth floatation process

differences in solubility.[141] In this process, a mixture in solution is allowed to crystallize, either through evaporation or by a changing the temperature. The precipitate will contain more of the least soluble substance.

The process has to be repeated an enormous number of times to get high purity. For example, REE bromates had to be crystallized for four years daily to obtain good quality holmium. And fractional crystallization was repeated a staggering 15,000 times to get decent quality thulium, which even then, still contained traces of other REEs.

Ion Exchange

The ion exchange method was first used during Second World War as a way to separate fission products obtained from nuclear reactors. In this process, a solution containing a REE mixture is filtered through zeolites or synthetic resins that act as cation exchangers. Various

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[140] Centrifugal force is not a gravitational force, I know, but I have to use terms in common usage.

[141] Although the technique was often used by chemists before the 20th century, credit for developing it to the point where kilograms of REEs could be produced is given to Charles James (1880–1928) professor of chemistry (and his undergraduate students) at the University of New Hampshire. All but forgotten today, James was well known and highly respected by his contemporaries. He published more than 60 papers on rare earth chemistry. American Chemical Society (ACS) webpage, *Separation of Rare Earth Elements*, 2012

solutions are then used to wash out the elements one at a time. Each fraction is mixed with acid to create an oxalate, which is heated to form the oxide.

Ion exchange, like fractional crystallization, is a long and laborious process, but it was better than any other method that had come before. It continued to be the only practical method of bulk separation of REEs until the 1970s.

Solvent Extraction

Solvent extraction uses chemicals to break down the components of the concentrate. Those materials that are more soluble, or react more readily to a particular acid or base, get separated from the rest. The separated materials are then removed, and the process begins all over again with the introduction of more chemicals to leach out more components. For REEs, these steps need to be repeated again and again… sometimes hundreds of times, depending on which REE is being extracted. The chemicals involved are extremely hazardous, and are usually required to be hot; they include concentrated sulphuric acid, ammonium hydroxide, sodium hydroxide, and hydrochloric acid.

Processing plants use a cascade of dozens of different tanks and machines for mixing, settling, filtering and evaporating all the various solutions in a continuous stream. The time required for solvent extraction can vary widely; it can be very lengthy in some cases where materials need to be allowed to mix and sit for a time. A final step in the process may be calcination—the use of ovens, induction furnaces, and arc furnaces to heat up and drive off volatiles and reduce carbonates and other compounds to oxides.

Chemical Dissolution Equipment

Reduction to metals

The end products of the separation processes are usually REOs of varying degrees of purity. Some applications for REEs however, require them to be in a pure metallic form, and this calls for further refining and separation. Again, this is no easy task, and a variety of techniques are used, sometimes in the same processing operation.

High Performance Centrifugal Partition Chromatography

From Bene Technology Co. brochure

One common technique is metallothermic reduction, which uses very highly electropositive metals like sodium and calcium in a molten state to reduce the REOs. Other extraction techniques are sorption using specially-designed resins; vacuum distillation, a method that exploits

difference in melting points and vapor pressures; mercury amalgamate oxidation-reduction, a modern version of an old technique developed for extracting silver; and high-performance centrifugal partition chromatography (HPCPC: a flow-through laboratory technique that could be scaled up. It exploits differences in partition coefficients in two immiscible liquids).

It is no surprise that REE processing plants cost hundreds of millions of dollars, require skilled labour to operate them; and create numerous environmental headaches. ◊◊

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Manuscript prepared as a term paper submission GEOL 300 at Vancouver Island University, April 5, 2013