Rare earths from supernova to superconductor

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Abstract

The origin, geological evolution, mineral deposition and uses of rare earth
elements (REE) are discussed. It is shown how their nuclear, geochemical and
chemical properties influence their behaviour in geological and industrial processes.

Analysis is critical and the appropriate method has to be selected carefully. A
geochemical and chemical insight is required to achieve the analytical aims which
often require concentrations from ppm to 50% to be determined. Significant
interferences exist. Various methods are reviewed.

INTRODUCTION

This paper aims to set the stage for several papers on the analysis of rare earth elements at this conference.
As these methods are many and the detailed papers much more comprehensive, I shall deal mainly with
rare earth geochemistry, extraction and technology, to explain why so many scientists and engineers
need to analyze materials for the rare earths (ref. 1).

More than for any other group of elements, the imprint of cosmic and geological processes is indelibly
stamped on rare earth minerals and concentrates. I shall discuss these natural imprints in an attempt to
remind the chemist and engineer that all our mineral resources spring ultimately from Mother Earth
which in turn is a minor child of the solar system and the galaxy.

RARE EARTHS IN THE PERIODIC TABLE AND THEIR BONDING ELECTRONS

The Rare Earth elements belong predominantly to the Lanthanide Group of the periodic table, having
atomic number 58 to 71 (Table 1). "Rare Earths" is a misnomer as these elements are neither rare, nor
earths, but the chemists who first isolated them as oxides named them thus to distinguish them from
alkaline earth elements like Mg, Ca and Sr. The lighter element yttrium has such similar properties to
the lanthanides that it is usually included as a rare earth element. The other Group IIIB element scandium
has sufficiently distinct chemical and geochemical character that it has escaped from its 1968 formal
inclusion in the rare earth elements by the International Union of Pure and Applied Chemistry.

The lanthanides are usually depicted below the main periodic table as they are a transition group, all
having two electrons in the outermost 6s orbital. As the atomic number increases from lanthanum to
lutetium the 4f orbitals inside the electron orbital structure are filled (Table 2). Losing three electrons
gives each rare earth a stable, xenon-like outer electron structure, which explains why they all have
remarkably similar chemical properties and normally form trivalent ions. Only two rare earth elements
can form different ions in nature: Ce^{4+} and Eu^{2+}. The rare earths are lithophile (rock-loving) because their
ions prefer to enter ionic silicate or oxide mineral structures rather than covalent sulphide or metallic
compounds.

Table 1 *The rare earth elements and Group IIIA of the periodic table*

Atomic No.	Symbol	Comments
21	Sc	Unlike lanthanides
39	Y	Similar to holmium
57	La	The first lanthanide
58	Ce	Can form Ce^{4+}
59	Pr	Light REEs 57–62
60	Nd	
61	Pm	Short lived radio-isotope
62	Sm	
63	Eu	
64	Gd	Can form Eu2+
65	Tb	Heavy REEs 64–71
66	Dy	
67	Ho	
68	Er	
69	Tm	
70	Yb	
71	Lu	The last lanthanide

Table 2 *Electron configuration of some rare earth element atoms and ions*

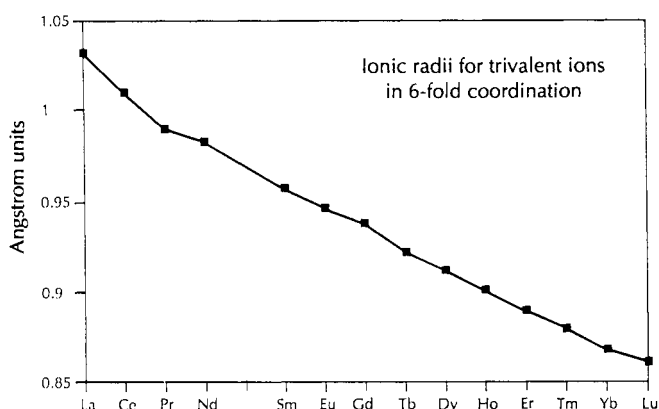|	Neutral atom	2 + cation	3 + cation	4 + cation
La	[Xe]5d^{1}6s^2		[Xe]	
Ce	[Xe]4f^{1}5d^{1}6s^2		[XE]4f^1	[Xe]
Pr	[Xe]4f^{3}6s^2		[Xe]4f^2	
Nd	[Xe]4f^{4}6s^2		[Xe]4f^3	
Eu	[Xe]4f^{7}6s^2	[Xe]4f^7	[Xe]4f^6	
Gd	[Xe]4f^{7}5d^{1}6s^2		[Xe]4f^7	
Ho	[Xe]4f^{11}6s^2		[Xe]4f^{10}	
Lu	[Xe]4f^{14}5d^{1}6s^2		[Xe]4f^{14}	

FIGURE 1. Ionic radii of the lanthanide group of rare earth elements, illustrating the lanthanide contraction (data from ref. 3)

In the crystal lattice sites of minerals the rare earths exhibit the lanthanide contraction, depicted in Figure 1. This decrease in size of the trivalent rare earth ions with increasing atomic number is explained by shielding, whereby the electrons defining the radius of the ion are attracted more strongly by the increasing number of protons in the nucleus. The lighter element yttrium behaves identically to holmium, which has the same ionic radius.

NUCLEOSYNTHESIS AND THE ODDO–HARKINS EFFECT

Our sun and other stars emit light which on spectral analysis reveals that they consist mainly of hydrogen and helium, with minor amounts of all the other elements. Helium is being produced by the nuclear fusion of hydrogen inside them, but stars are not able to make elements more massive than carbon. Supernovae implosion-explosion events are the only likely producers of heavy elements such as the rare earths. Such events took place in our corner of the galaxy from fifteen to five billion years ago. They produced huge fluxes of neutrons, which were captured by atomic nuclei and subsequently decayed to proton plus electron, thus increasing both the atomic number and mass number of the nuclei by which they had been captured. The stamp of this pre-solar system process is seen in the rare earth element analyses of all terrestrial, lunar and meteorite samples. Rare earth concentrations of two terrestrial materials are shown in Figure 2, plotted against atomic number of the fourteen elements lanthanum to lutetium. The even atomic-numbered elements such as cerium, neodymium, and samarium are an order of magnitude more abundant than the adjacent odd-numbered elements. This "Oddo-Harkins" effect results from the even-numbered elements with lower neutron-capture cross-sections being less likely during neutron-flux events to capture another neutron and be transformed into the next-higher element.
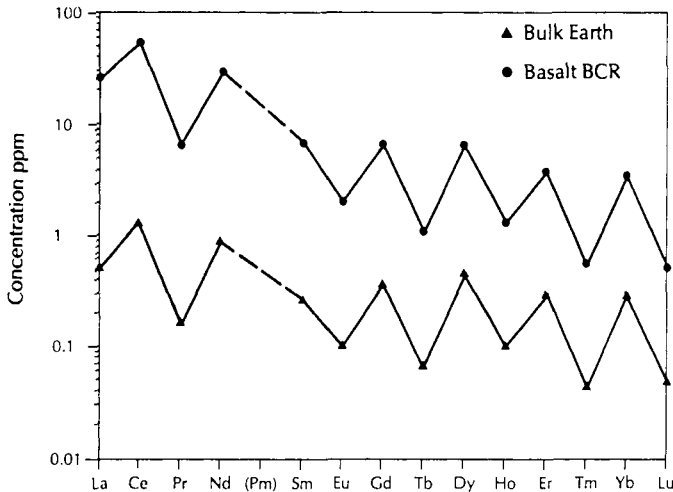
FIGURE 2.
Rare earth analysis of international rock standard BCR-1 compared with an estimate of the bulk earth composition according to ref. 4
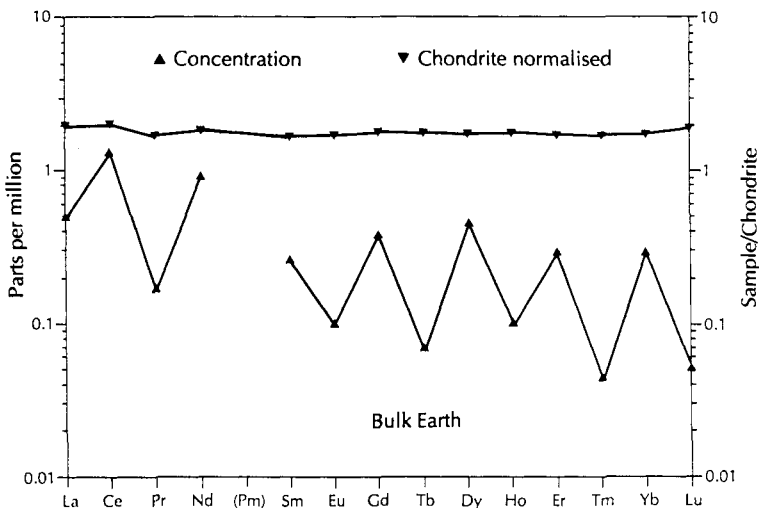

FIGURE 3. Bulk earth composition plotted against logarithmic (parts per million) and chondrite normalised scales. Dividing the sample concentration by that of chondrite meteorites (refs 5, 6) yields a smooth chondrite-normalised rare earth element profile

Note the logarithmic abundance scale and that the light rare earth elements cerium and lanthanum constitute the bulk by mass of the rare earth group, while the heavy elements gadolinium to lutetium have very low concentrations.

The Oddo-Harkins effect makes it difficult to work with rare earth element profiles as plotted in Figure 2, so data is usually plotted on Masuda-Coryell diagrams normalised using the concentrations in chondritic meteorite, which closely represents the primordial solar system material (refs 4 to 6). Thus as shown by Figure 3, pre-solar system processes are cancelled out, allowing us to concentrate on those which have operated since the earth formed some 4650 million years ago.

BASALT GENESIS BY MELTING OF THE MANTLE

Trivalent rare earth ions with radii about one angstrom, are the same size as divalent calcium ions. So the rare earth elements fit into the crystal lattices of calcium-bearing rock forming minerals such as pyroxene $CaMgSiO_3$ and plagioclase $CaAl_2Si_2O_8$. But because of their higher charge and crystalline energy, if such minerals are in equilibrium with a silicate melt the rare earths are concentrated in the melt and are thus called incompatible elements. When a portion of the earths mantle, which is close
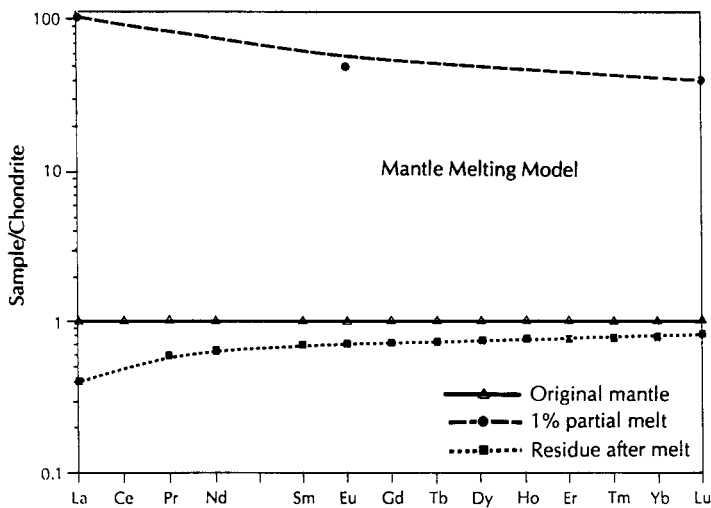
FIGURE 4.
A simplified model (ref. 7) showing the calculated rare earth profiles resulting from the melting of chondritic mantle to produce 1% basaltic partial melt liquid and 99% residue

in composition to chondrite meteorites, melts to form a basaltic liquid, the light rare earths are more strongly concentrated in the basaltic melt, as shown by a model in Figure 4, (ref. 7). The mantle peridotite which remains solid becomes depleted in light rare earth elements, while the basaltic melts produced from it show both overall and light rare earth enrichment.

Basalt makes up the crust beneath the oceans. The continental crust was derived from it by a second stage of melting in subduction zones. The rare earth element profiles of all igneous rocks reflect (a) the signature of their source rocks and (b) the signature of their melting system and proportion of melt produced.

THE CONTINENTAL CRUST

The crust on which we live and work is mainly granite, covered by sedimentary rocks derived from its weathering and erosion. Mantle peridotite contains about 40% silica, basalt 50% and granite 60% and granite is also enriched in alkali elements at the expense of Mg Fe and Ca. Models based on trace element partition coefficients show that to derive granitic rocks from the mantle, two or more stages of melting are required, producing first basalt and then granite. The rare earths play an important role in constraining models for the genesis of the continental crust. A typical granitic rare earth element profile is shown in Figure 5. The features which it shows are: overall 40 times enrichment relative to chondrites (controlled by the degree of melting), a factor five enrichment of light relative to heavy rare earths (controlled by the mineralogy of source rocks), and a negative europium anomaly (reflecting plagioclase fractionation). Plagioclase has a strong affinity for the reduced form of Eu^{2+}, depleting it in liquid magmas from which it crystallises. This feature which is useful to geologists, is not popular with mining houses as will be shown below.

Soils are derived from rocks by weathering, and they have rare earth element profiles which reflect their provenance, while Ce and Eu anomalies may develop due to redox reactions during paedogenesis. In Figure 6 the rare earth profiles for some French wines, analyzed by direct aspiration ICPMS, show large differences in rare earth profile related to differences in soil composition. However one should bear in mind that some fertilizers contain high concentrations of rare earths from carbonatite apatite!

Inductively coupled mass spectrometric (ICPMS) and thermionic isotope dilution mass spectrometric (IDMS) analysis.

To do geochemical research on rocks and soils one needs an analytical technique which can attain routine detection limits close to 0.01 parts per million in solid samples, and determine most of the fourteen lanthanides. Inductively-coupled plasma mass spectrometry is one suitable technique as it

Oribi Gorge Granite

Light

R E E

Enrichment

Europium anomaly

Sample/Chondrite
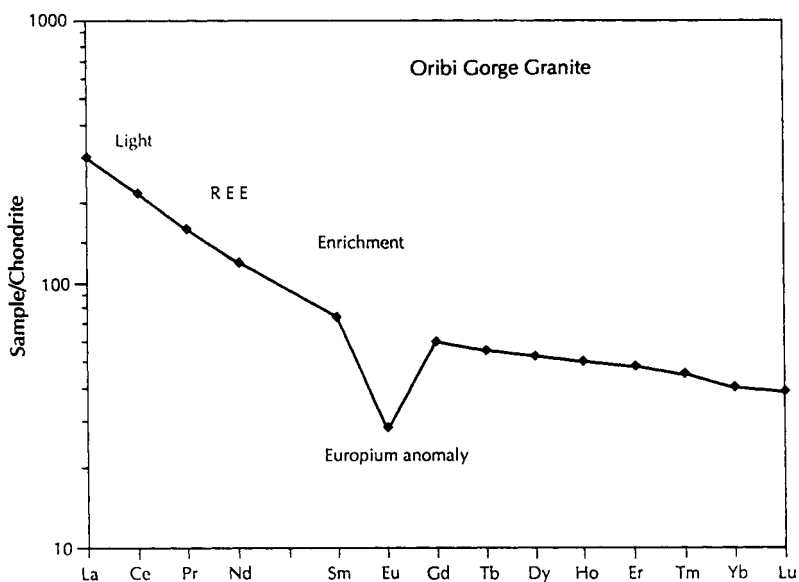
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

FIGURE 5. Chondrite normalised rare earth element profile of a typical granite sample from Oribi Gorge, southern Natal, showing light rare earth enrichment and a negative europium anomaly. Data from Thomas and Cornell in prep.

French Wines

Wine/Chondrite

■ Sancerre
● Pommard
◆ Pomerol
▲ St Emilion

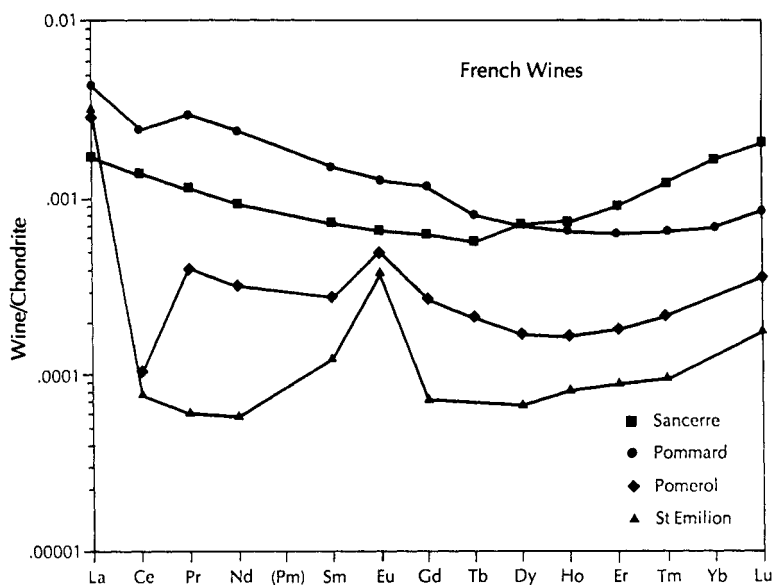La Ce Pr Nd (Pm) Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

FIGURE 6. Rare earth profiles for four French wines, analyzed using ICPMS by E. McCurdy *et al.*, data supplied by VG Elemental, Winsford, Cheshire, UK

resolves each isotope of the rare earth mass spectrum as shown in Figure 7, allowing interference-free detection of part-per billion levels (ref. 8) Samples are normally introduced to the plasma in solution, however a laser ablation device now allows the direct analysis of solids. ICPMS instruments may drift by more than 10% during a run, due to the build-up of solids in the interface. Internal standards are unavoidable, two elements of different mass such as indium and rhenium being added to the solutions to correct for matrix effects and drifts in both overall intensity and mass fractionation. Precision using internal standards is normally better than 5%, but can be greatly reduced using isotope dilution mass spectrometry in which a purified isotope tracer is added to change the isotope ratio of an element in the sample. Isotope dilution is more commonly employed with thermionic mass spectrometers such as are used in dating laboratories. However these instruments are expensive and samples require labour-intensive chemical separation before analysis (ref. 9).
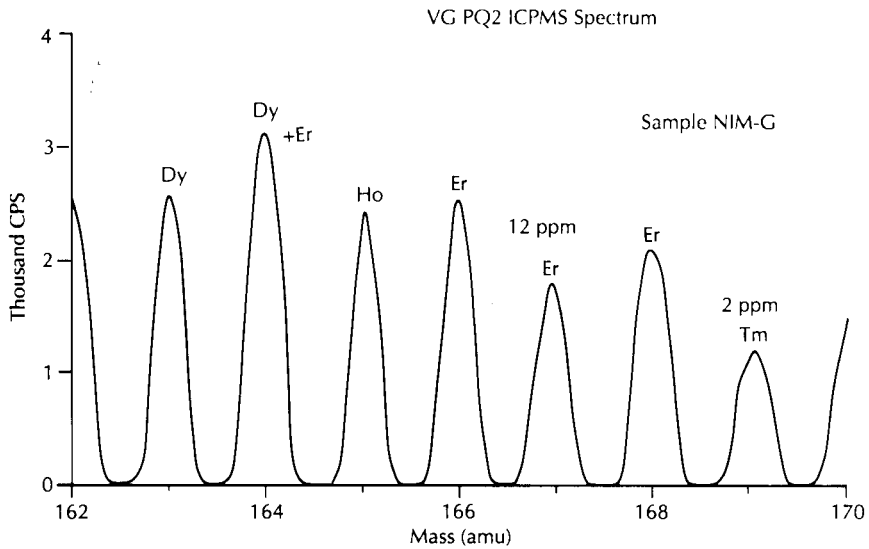
VG PQ2 ICPMS Spectrum

FIGURE 7. ICP mass spectrum showing some of the isotopes of the heavy rare earth elements dysprosium, erbium and thulium, for the rock standard sample NIM-G by inductively coupled plasma mass spectrometry. The only significant spectral overlap is between the isobars ^{164}Dy and ^{164}Er

NEW METHODS OF DATING ROCKS

No less than six of the rare earth elements have one or more radioactive isotopes, but as their half-lives range from 10^{10} to 10^{16} years, it has not been feasible to use their radioactive decay as geological clocks, because they produce such small amounts of daughter isotopes in geological time spans between 10^6 and 10^9 years. However as more stable thermionic mass spectrometers were developed, three new dating methods have been proven: samarium-neodymium, lutetium-hafnium and lanthanum-cerium. Sm/Nd has been the most successful. The Sm/Nd technique has now been widely used in dating some of the worlds oldest rocks, notably in southern Africa the Ancient Gneiss Complex of Swaziland (ref. 10) at 3417 _34 Ma, and the volcanic rocks of the Onverwacht Group in Barberton Mountain Land at 3540 _30 Ma (ref. 11). This method also provides information about the source from which igneous rocks were derived which can be used in models describing the structure and origin of the mantle and crust of the earth.

RARE EARTH ORE MINERALS

In peridotite and basalt, rare earth elements usually total less than 100 parts per million spread evenly throughout most of the major minerals feldspar and pyroxene. They occupy a small proportion of the crystal lattice positions of major elements like calcium. In granitic melts rare earths encounter new minor minerals not found in basalts, such as apatite $Ca_5(PO_4)_3(OH)_3$ and zircon $ZrSiO_3$, which have crystal lattice positions more inviting to rare earths than those of common minerals. As a result these trace minerals take up larger proportions of the available rare earth elements. In the trace-element rich fluids which remain after most of the magmatic liquid has solidified, rare earth minerals like monazite may form in coarse-grained pegmatites. This important ore mineral, a cerium-thorium phosphate, contains all the other rare earths, decreasing with increasing atomic number as shown in Figure 8. Monazite occurs in small amounts in most granitic rocks, and when they weather and are carried to the sea in rivers, the monazite grains move with them. As monazite grains are denser than silicate minerals, they are concentrated with other heavy minerals like ilmenite $FeTiO_3$ and zircon on beaches and dunes. When such placer mineral deposits are mined for their titanium content, for example in Australia and Natal, South Africa, the monazite is also extracted and sold as a by-product.
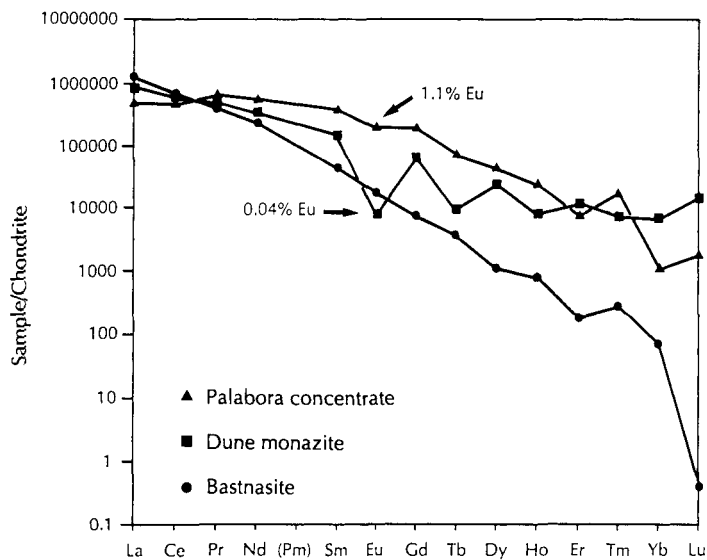
FIGURE 8. Chondrite normalised rare earth profiles for a typical dune deposit monazite, compared with Mountain Pass bästnasite (data from ref. 15) and a rare earth concentrate from the Palabora carbonatite (data from FEDMIS, pers. comm.) show significant differences in europium concentration

Monazite was originally mined for thorium coatings on incandescent gas lamp mantles. The rare earth content is now more valuable, but monazite has two disadvantages as a rare earth ore. Its radioactivity requires precautions in handling and extraction. Secondly, because monazites form late in the igneous crystallization sequence, they contain little europium as shown in Figure 8, because it has already been taken up by plagioclase. Europium is the most important rare earth element in today's market, contributing to the development of square-eyes in our children.

The other major rare earth ore mineral is the carbonate bastnäsite, which is found mainly in one carbonatite intrusive plug at Mountain Pass, California. This is the major producer of rare earth minerals, about 20 000 tons per annum and contributed to rare earth technology in an unusual way. The company which owned it had no market for bastnäsite, so invested heavily in research. This paid off when they discovered that europium could form a highly efficient red phosphor for television screens; every colour TV today contains about one rands worth of europium, much of it coming from Mountain Pass. The much higher Eu content of Mountain Pass bastnäsite shown in Figure 8 makes it a more valuable ore than monazite, and it also has low thorium.

Apatite is a common calcium phosphate mineral also found in carbonatites which can yield a rare earth concentrate. The analysis shown in Figure 8 is from Palabora, a carbonatite pipe in the eastern Transvaal, South Africa. Although rare earths are only minor constituents of this apatite, the company which mines it for phosphate fertilizer separates the rare earths as a by-product. This product also has a favourable europium concentration as plagioclase is absent from the carbonatite system.

X-RAY FLUORESCENCE ANALYSIS AND GEOCHEMICAL PROSPECTING

Scanning electron microscope X-ray spectra of two rare earth phosphate minerals from a dune sand mine, monazite and xenotime are shown in Figure 9. While monazite shows large peaks for the light rare earths, xenotime has a smaller lattice site which accommodates only yttrium and the heavy rare earths. The X-ray technique clearly distinguishes these minerals, but overlaps of the fourfold L-spectral lines of the individual elements makes quantitative analysis difficult. The four most abundant light rare earth elements La, Ce, Nd and Sm can be determined with high-resolution wavelength-dispersive spectrometers at levels above ten ppm in rock and ore samples, but even with group separation and concentration methods (ref. 12) elements like Eu remain hidden in the background.
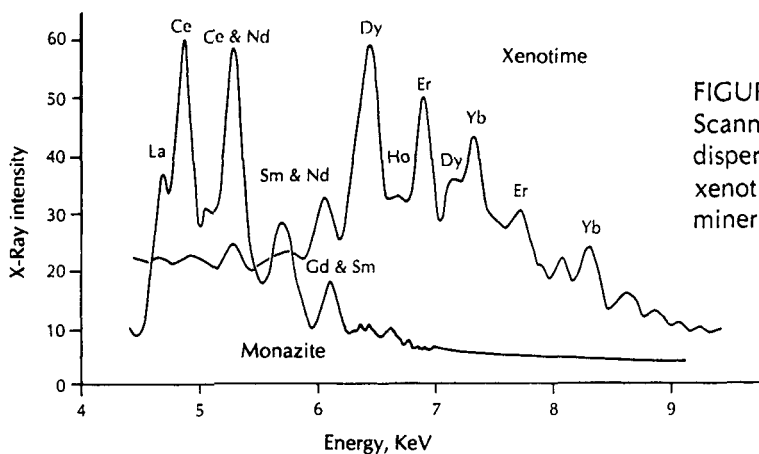
FIGURE 9.
Scanning electron microscope energy-dispersive X-ray spectra of monazite and xenotime, two rare earth phosphate minerals

X-ray methods are thus not used to determine rare earth profiles, but because of their low cost and rapid turnround, are ideal for prospecting if only La, Ce and Y (representing the heavy rare earths) are required. Stream sediments and soil samples can be analyzed in large numbers, revealing anomamous target regions in which prospecting may be concentrated (ref. 13). Once a deposit has been discovered and delineated, more comprehensive and expensive analytical methods come into play.

GROUP SEPARATION AND LOW-TECHNOLOGY USES

Rare earth minerals are normally sold as concentrates containing more than 90% of the ore mineral. The first step in extraction aims to produce an undifferentiated rare earth product containing mostly cerium and lanthanum with minor amounts of all the others according to their proportions in the ore mineral. The group extraction is achieved by reaction with either caustic soda or with sulphuric acid. If monazite is the feedstock to this process, radioactive thorium becomes an effluent and represents an environmental problem (ref. 14). Such combined rare earth products can be used in applications where any one of the rare earth elements has the desired effect, for example the production of steel alloys, in catalysts or as an abrasive for glass polishing. The term "misch metal" is used for the hard, silver rare earth metal, which has the intimidating property of spontaneous combustion in air. It is used in lighter flints as a spark-inducer, as well as in alloy metallurgy (ref. 15). I once had an exciting experience trying to weigh cerium metal powder to make a standard solution, whilst it, once free of the argon it was stored in, was bent on becoming an oxide as quickly as it could!

THE WORLD MARKET FOR RARE EARTHS AND ESTABLISHED USES

About 2.2 million tons of rare earths have been produced in the past century (Figure 10); present annual production is about 50 kilotons. Steenkampskraal monazite mine at Van Rynsdorp in Namaqualand, South Africa was a major producer during the second world war but was quickly mined out. With the rapid growth in demand for rare earths geological exploration has also increased and the official world reserves of 50 million tons would last a thousand years at the present rate of consumption. Specific rare earth elements are much more expensive than the group concentrates. For example "cerium" polishing powder, containing all the other rare earths costs 0.31 US cents/gram, while 99.9% pure cerium oxide is 2.1 c/g and 99.9% pure metal is 19c/g (ref. 16, standard container loads). Prices quoted by Johnson Matthey Ltd. for one gram of the individual rare earth metals range from US $5 (lanthanum) to $140 (europium) and $350 for lutetium (probably because there is little demand and the separation is costly). These prices are comparable with those of gold, platinum and silver, so in this respect the rare earths are precious metals! As with precious metals, the price depends on demand, and overproduction will probably lead to massive price reductions.

Some interesting aspects of present-day use are: Rare-earth zeolite catalysts are used for "cracking" crude oil to produce shorter-chain molecules in petrol refining. The white blebs on the sides of self-cleaning ovens are rare earth oxides which promote the oxidation of fat. Spectacles, telescope mirrors and television screens are polished with "ceria" polishing powder. In glass manufacture the unwanted
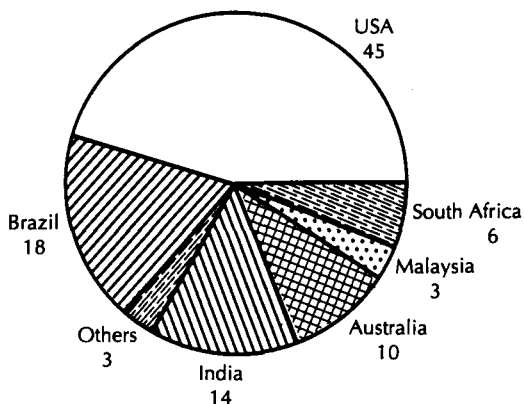
FIGURE 10. Global rare earth element production (mt) of the major producing countries 1885–1980, according to ref. 15. Total production was 1.7 Mt. Most of South African production was from the now-defunct Steenkampskraal monazite mine
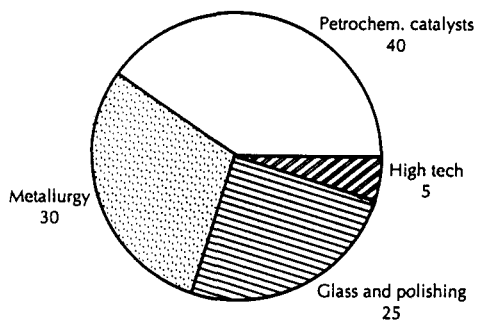
FIGURE 11. Rare earth element usage by mass, updated from ref. 15. The 5% used in high-tech applications is the fastest-growing and highest-value sector

blue colour of ferric Fe^{3+} iron is removed by oxidizing it to the ferrous Fe^{3+} state using ceric oxide CeO_2 (ref. 15). The europium-based red phosphor for television screens allowed manufacturers to increase the relative brightness of the other colours by 40%. The development of all these products required a mix of applied chemistry and crystallography, with a sprinkling of physics, backed up as always by analytical chemistry.

Although industrial consumption should increase exponentially, the inexorably high demand for europium for TV screens seems sure in the medium term to be the major factor in the supply and demand mechanism which determines the price of rare earths.

ELEMENT SEPARATION FOR HIGH-TECH PRODUCTS

The present uses of rare earths are summarised in Figure 10. The "high tech" sector represents a rapidly growing new market, which requires individual rare earth elements at purities ranging from 60 to 99.999% (ref. 15). Upgrading rare earth ores to high-purity metals adds orders of magnitude to their value, as shown by Figure 12. Analytical control of the purity of pure rare earth products requires
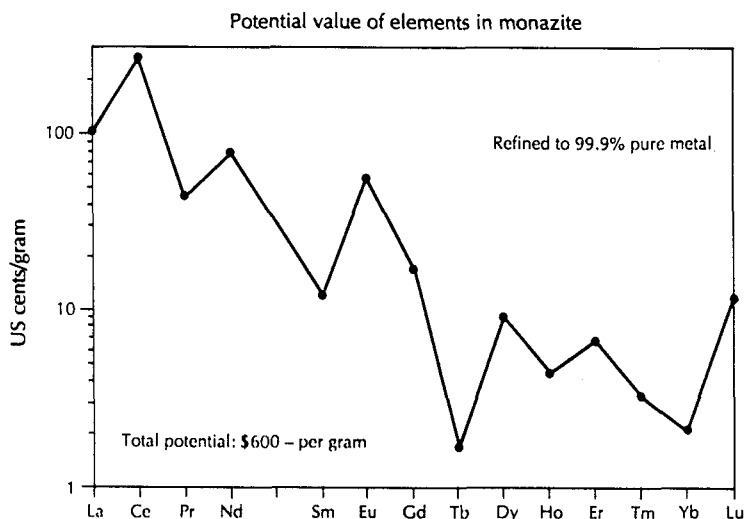

FIGURE 12. The potential value of each element proportion in one gram of monazite if refined to 99.9% pure metal, in US cents

techniques which can detect low impurity levels in essentially 100% of a single oxide or metal. Optical or mass spectrometry is most commonly used, the solid sample being vaporised by either spark, DC arc or laser ablation. The laser ablation ICPMS can determine impurities at the sub-ppb (ng/g) level.

To obtain such products from the group-separated material, the subtle differences between the elements have to be exploited. Europium and cerium are usually converted to the divalent or tetravalent ions respectively, to yield insoluble compounds which precipitate while the trivalent rare earths are still soluble. The other rare earths are usually purified by extraction in organic solvents, which process has the advantage of being amenable to continuous-flow operations (ref. 17). These techniques are well-known and used in the first-world economy, notably in the USA, EC and Japan. Although South Africa now produces both monazite concentrates from dune mines and a rare earth group concentrate from Palabora apatite, the major value-adding process of separation into pure oxides and metals is still done in true first world countries. There seems little prospect of rare-earth refining industries developing close to the mines unless a major cost-saving breakthrough is made by MINTEK or other mineral technology groups.

Analytical methods using chromatographic separation: Ion chromatography and ICP atomic emission spectrography

In ion chromatography the operator passes a sample in solution though an ion-exchange column in which the rare earths are separated because of their slightly differing partition coefficients. The elements are detected as conductivity peaks on emerging from the column. This method uses relatively inexpensive equipment and has proved successful for rock analysis (ref. 18). However it cannot easily handle the large differences in concentration between adjacent elements produced in industrial refining. Another method which depends on a similar separation for rare earth analysis is inductively coupled plasma atomic emission spectrography (ICPAES). The major elements such as iron present in most samples cause severe overlap interferences with many of the rare earths in the optical spectrum. Group separation using ion exchange columns is the salvation of this method which has dynamic range and sensitivity similar to that of the more expensive ICPMS (ref. 19). However the skilled manpower needed for separation is a major cost factor. Note also that one may easily produce negative cerium anomalies during separation by allowing the ion exchange resin to dry out in the presence of nitric acid; the resin retains Ce^{4+} from subsequent next samples.

RARE EARTHS AS A FUTURE RESOURCE

Many new applications of rare earth elements are currently being developed. One which is already far advanced is the production of permanent magnets based on samarium or neodymium, which are more than five times stronger than conventional alnico magnets. These are used in small motors and appliances, particularly where weight savings are important in car and aircraft manufacture. Production in 1988 was about 300 tons per annum and is rapidly increasing (ref 19). Material scientists are using rare earths to stabilize crystal structures like cubic zirconia, and to make new compounds such as yttrium-aluminium garnet (YAG) a laser generator and yttrium-iron garnet (YIG) for microwave systems.

An exciting chapter in rare-earth technology followed the discovery by Bednorz and Müller (ref. 20) and subsequent workers of high-temperature superconductors comprising lanthanum barium copper oxides such as $La_{2-x}Ba_xCuO_4$ (Figure 13). These have no resistance to electric current at 90K or -183_C, easily attainable using cheap -195_C liquid nitrogen, while current superconductors need expensive liquid helium at -269_C. This discovery led to an explosion of research and hasty papers in Nature, with massive funding being channelled into new multidisciplinary research groups. Crystallography suddenly became fashionable: the unusual prospect arose of Nobel prizes for materials scientists, the promise of superconducting power transmission cables which would save 50% of power losses in national grids, and other advances such as liquid-nitrogen-based superconducting magnets for medical body-scanners and nuclear research accelerators.

Table 3 *Comparsion of some analytical methods for rare earth elements.*
One US dollar equals approximately 3 SA Rands

Technique	Routine detection limit in solid sample	Number of elements determined	Operator time (including sample preparation and calculation)	Instrument time (including standards)	Total analysis time from submission to results	Cost of instrument 1992 in in South Africa	Cost per analysis in South Africa 1992
Units	ppm (ng/kg)		hours	hours	days	R100 000	S A Rands
Neutron activation analysis	5–0.1	8–10	2	4	36	2.5	150
Inductively coupled plasma mass spectrometry	0.1–0.01	15	2	0.3	2	10	150
Inductively coupled plasma atomic emission spectrometry	0.5–0.005	12–15	6	0.2	7	3	100
Ion chromatrography	0.1–0.01	12	4	1	2	2	150
Isotope dilution (thermionic) mass spectrometry	1–0.01	8–10	8	4	7	40	500
X-ray fluorescence spectrometry	10	5	2	1	1	10	50

Two facts have emerged as the dust settles: copper, not lanthanum, forms the basis of the superconductor, the other cations which may include other rare earths, bismuth and thallium, are needed simply to provide the right framework in the perovskite structure for copper oxide planes to carry the current without resistance. Secondly, there are technical problems in making long, superconducting cables which can transmit significant amounts of electrical power. This is because of the difficulty of maintaining superconductivity across grain-boundaries, and because these ceramic materials are brittle and fracture easily. In this area of endeavour analytical methods are proving crucial, to introduce and monitor the desired levels of impurities and in determining the crystal structures using electron microscopes and X-Ray or electron diffraction. It remains to be seen whether rare earths form part of the final product of this unexpected technological breakthrough, which is a good example of a spin-off from "pure" research.
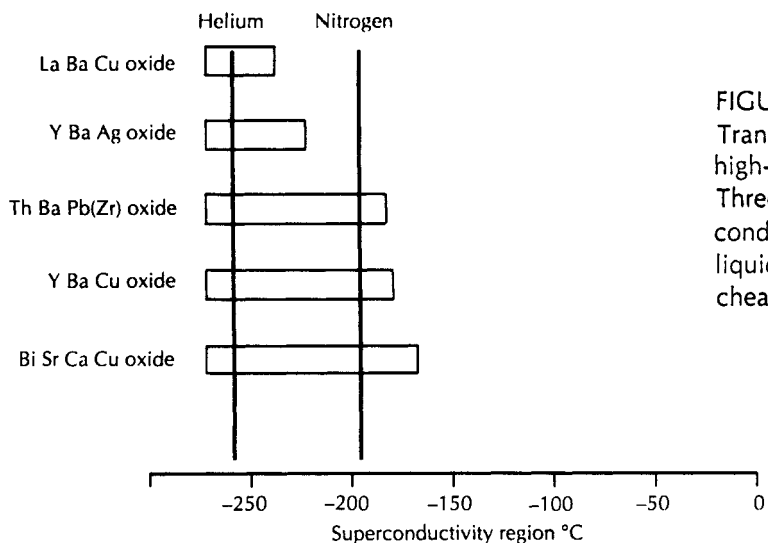
FIGURE 13.
Transition temperatures of some high-temperature superconductors. Three of these materials are super-conducting when immersed in liquid nitrogen, which is much cheaper than liquid helium

WHICH METHOD TO USE?

In Table 3 I have summarised some important features of several techniques used for rare earth element analysis. As I have pointed out during above each method has its applications to one or other area of endeavour. For many applications it is probably better to pay an already expert laboratory to do the analysis than to embark on a long and expensive learning curve. If one is contemplating in-house analysis of rare earths, the cost and reliability of equipment are major factors, however sophisticated equipment cannot overcome the need for an expert analyst who has the time to roll up his sleeves, do battle with suppliers and get his test-tubes wet!

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