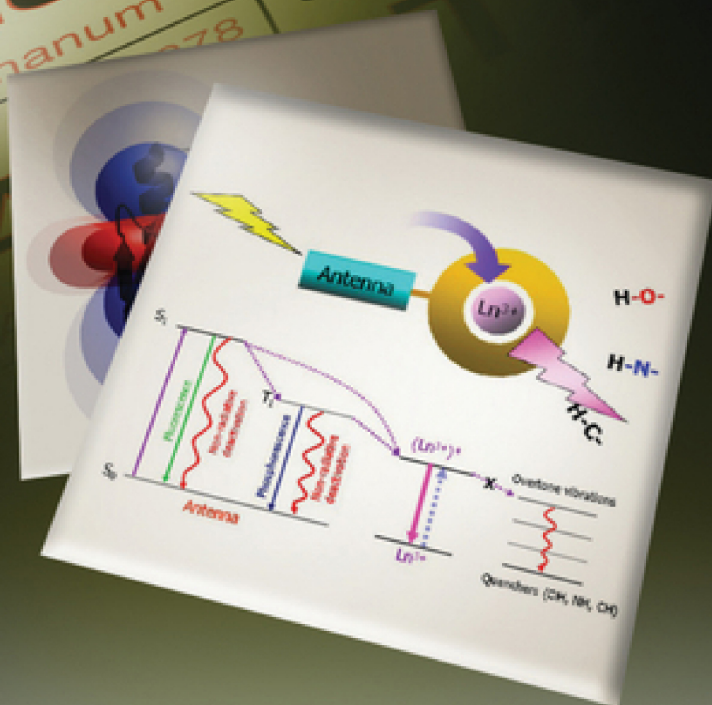



Editor
David A. Atwood

The Rare Earth Elements

Fundamentals and Applications



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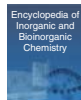


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THE RARE EARTH ELEMENTS:

F u n d a m e n t a l s a n d A p p l i c a t i o n s

Editor

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Series Preface

The success of the *Encyclopedia of Inorganic Chemistry* (EIC), pioneered by Bruce King, the founding Editor in Chief, led to the 2012 integration of articles from the *Handbook of Metalloproteins* to create the newly launched *Encyclopedia of Inorganic and Bioinorganic Chemistry* (EIBC). This has been accompanied by a significant expansion of our Editorial Advisory Board with international representation in all areas of inorganic chemistry. It was under Bruce's successor, Bob Crabtree, that it was recognized that not everyone would necessarily need access to the full extent of EIBC. All EIBC articles are online and are searchable, but we still recognized value in more concise thematic volumes targeted to a specific area of interest. This idea encouraged us to produce a series of EIC (now EIBC) Books, focusing on topics of current interest. These will continue to appear on an approximately annual basis and will feature the leading scholars in their fields, often being guest coedited by one of these leaders. Like the Encyclopedia, we hope that EIBC Books continue to provide both the starting research student and the confirmed research worker a critical distillation of the leading concepts and provide a structured entry into the fields covered.

The EIBC Books are referred to as “spin-on” books, recognizing that all the articles in these thematic volumes are destined to become part of the online content of EIBC, usually forming a new category of articles in the EIBC topical structure. We find that this provides multiple routes to finding the latest summaries of current research.

I fully recognize that this latest transformation of EIBC is built upon the efforts of my predecessors, Bruce King and Bob Crabtree, my fellow editors, as well as the Wiley personnel, and, most particularly, the numerous authors of EIBC articles. It is the dedication and commitment of all these people that is responsible for the creation and production of this series and the “parent” EIBC.

Robert A. Scott
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November 2012

Volume Preface

The rare earth elements (REE) include lanthanum and the f-block elements, cerium through lutetium. Scandium and yttrium are included in this group as they have ionic radii similar to the lighter f-block elements and are found together in the same ores. The chemical similarities of the 17 REE make them unique in comparison to the other metals in the periodic table where two adjacent elements in a period typically have significantly different chemical properties. This makes the REE relatively difficult to separate from one another, although there are minerals where the lighter (La–Eu) and heavier (Y and Gd–Lu) REE are concentrated. REE research has benefited from this similarity, however, as compounds and materials formed with one REE can often be replicated with one or more of the other REE.

The sequential filling of the f orbitals beginning with cerium gives the REE very unique electronic, optical, luminescent, and magnetic properties. Over the past several decades these properties have been utilized in a wide range of synthetic, catalytic, electronic, medicinal, and military applications. The REE are now found in a multitude of consumer products such as computers, cell phones, and televisions. REE are used in automotive catalytic converters, petroleum refining, lasers, fuel cells, light-emitting diodes, magnetic resonance imaging (MRI), hybrid electric vehicles, solar energy, and windmills, to name but a few examples. REE are not only ubiquitous in modern society; they will be of critical importance in achieving a carbon-free, sustainable, global energy supply.

The Rare Earths: Fundamentals and Applications provides the knowledge of fundamental REE chemistry necessary to understand how the elements are currently being used and how they might be used in the future. The book is organized to provide a comprehensive description of the breadth of REE chemistry in four sequential sections: fundamental chemistry (Chapters 1–12), important representative compounds (Chapters 13–30), examples of solid-state materials (Chapters 31–36), and current and potential new applications (Chapters 37–45). It is designed to provide students, instructors, academic researchers, and industrial personnel with a fundamental understanding of the electronic, chemical, and physical properties of the rare earth

elements. This knowledge may be used to understand the current use of the elements and, it is hoped, will inspire and encourage new developments. With the possibility that REE resources and supplies will become limited in the near future, some of the new REE developments should include reducing the environmental impacts related to mining and isolation, recovering and recycling the elements from existing products, finding elements and compounds that could be substituted for REE, and ultimately, designing products where the elements or product components can be readily and economically reused.

While this book describes many of the more important aspects of the REE, it would be impossible for a single volume to incorporate the vast number of compounds, materials, and applications that contain or utilize REE. New information will be addressed in future articles in the *Encyclopedia of Inorganic and Bioinorganic Chemistry (EIBC)*. For example, there will be new REE articles on mining and extraction, metals and alloys, similarities of the REE with elements in Groups 1, 2, and 13, computational studies, carbonate, silicate, and polyoxometallate solid state materials, single-molecule magnets, environmental speciation, recycling, and many others.

The Rare Earths: Fundamentals and Applications is an ideal starting point and foundation for educating students, instructors, academic researchers, and industrial personnel on the unique chemistry and applications associated with the rare earth elements. New EIBC articles will supplement the contents of the book and will provide information on a broader range of rare earth compounds, materials, applications, and new developments.

I am grateful to the many authors who made substantial contributions to the outline and content of this book while it was being organized. I am especially grateful to Simon Cotton for the excellent expert assistance, information, and ideas he provided throughout the process.

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May 2012

Geology, Geochemistry, and Natural Abundances of the Rare Earth Elements

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1 SUMMARY

The rare earth elements (REE) are trace elements in most geological settings and are of great utility in understanding a wide variety of geological, geochemical, and cosmochemical processes that take place on the Earth, other planets, and other planetary bodies (e.g., Moon, asteroids). The properties that lead to this importance include the following: REE are an extremely coherent group of trace elements, by geochemical standards, in terms of ionic radius, charge, and mineral site coordination, which makes them especially valuable for monitoring magmatic processes; slight variations in their overall refractory nature provides insights into early solar system high-temperature processes; the distinctive redox chemistries of europium and cerium result in unique insights into magmatic and aqueous processes, respectively; their generally insoluble character in geological settings and resistance to remobilization beyond the mineralogical scale

during weathering, diagenesis, and metamorphism makes them important tracers for characterizing various geochemical “reservoirs” (e.g., planetary crusts and mantles).

In addition to being of great value to general geochemistry investigations, the REE have proven of increasingly great commercial value. Modern applications involve many that are useful in high technology, including some of strategic/military use. Accordingly, understanding the geological conditions leading to REE concentrations that are sufficient for economically viable extraction is also seen as increasingly important.

This chapter addresses geological and geochemical factors that control REE distributions in rocks and minerals, both in the Earth and on other planetary bodies, and the processes that give rise to economic concentrations of REE in the Earth’s crust. We begin with a discussion of the fundamental geochemistry and cosmochemistry of REE. This is followed by describing processes that influence the distribution of REE in rocks and minerals and the geological

conditions that give rise to ore-grade concentrations. Finally, we characterize abundances and distributions of REE in various reservoirs, such as bulk solar system, bulk Earth, crust, oceans, and so forth, that are relevant to understanding the origin and evolution of the Earth.

2 INTRODUCTION

Geochemists have long recognized the misnomer associated with the REE, aptly captured in the title of one early paper, “Dispersed and not-so-rare earths.”¹ Although REE occur as trace elements in the vast majority of geological environments, their natural abundances in crustal rocks, mostly ranging from hundreds of parts per billion (terbium, holmium, thulium, lutetium) to tens of parts per million (lanthanum, cerium, neodymium), are not exceptionally low compared to many other elements. Thus, depending on the estimate, the most common REE, cerium, is approximately the 27th most abundant element in the continental crust of the Earth. Regardless of absolute amounts, the REE arguably are the single most important coherent suite of elements in nature for the purposes of interpreting a wide variety of geological processes for reasons discussed below. Accordingly, the absolute concentrations and embedded radiogenic isotopic systems (e.g., ¹⁴⁷Sm–¹⁴³Nd, ¹⁴⁶Sm–¹⁴²Nd, ¹⁷⁶Lu–¹⁷⁶Hf, ¹³⁸La–¹³⁸Ce) have been studied in exhaustive detail in a wide variety of rocks, minerals, and aqueous fluids on the Earth and other available solar system bodies.

Industrial uses of REE metals and compounds have expanded greatly over the past century, from the early application of mixing small amounts of cerium oxide with thorium oxide to produce incandescent gas light mantles, developed in the late nineteenth century, to being crucial components in a wide variety of cutting-edge technology applications.² Modern uses of the REE in high-technology applications include many of considerable strategic value.³ Accordingly, geological processes giving rise to ore-grade concentrations of REE are also of increasing interest.

The history of meaningful geological and geochemical research using REE dates from the pioneering work of Victor Goldschmidt and Eiiti Minami in 1935, who used X-ray spectrography to first determine REE abundances in rock samples—European and Japanese shale composites.⁴ At that time, most workers were of the opinion that relative REE distributions were not fractionated by geological processes and early differences in REE distributions noted between shales and meteorites were dismissed as analytical error. Modern REE geochemical research dates from the early 1960s with the development of rapid and precise instrumental techniques, notably radiochemical and instrumental neutron activation analyses pioneered by Larry Haskin, Roman Schmitt, and their colleagues.^{5,6} (Various rapid high-precision mass spectrometry methods such as thermal ionization isotope dilution

mass spectrometry and spark source mass spectrometry soon followed.) The seminal breakthrough of Haskin’s work was that REE distributions in shales were indeed significantly fractionated from meteorites, having higher abundances and relative enrichment of the light rare earth elements (LREE), lanthanum through samarium, thus opening the door to the modern phase of REE geochemical research, summarized here.

In this chapter, we are concerned with four major issues: (i) general geochemistry and cosmochemistry of REE; (ii) geological conditions giving rise to normal concentrations of REE in rocks, minerals, and natural waters; (iii) geological conditions giving rise to ore-grade concentrations of REE; and (iv) the abundances and distributions of REE in various geochemical and cosmochemical “reservoirs” that are relevant to understanding the origin and evolution of the Earth.

3 GENERAL GEOCHEMISTRY OF THE RARE EARTH ELEMENTS

3.1 Geochemical and Cosmochemical Classification

The REE consist of the Group 3 transition elements ²¹Sc, ³⁹Y, and ⁵⁷La and the inner transition (lanthanide) elements ⁵⁸Ce through ⁷¹Lu. As described in greater detail below, the REE are trivalent in all known geochemical systems with the exception of europium (which can also be divalent) and cerium (which can also be tetravalent). In geochemistry nomenclature, the term *rare earth elements* almost universally refers only to lanthanum, yttrium, and the lanthanides (i.e., La–Lu, Y), which differs from formal chemistry nomenclature, resulting in some confusion. Geochemists also subdivide REE into the light rare earths (LREE (La–Sm) and heavy rare earth elements (HREE; Gd–Lu) due to their contrasting geochemical behavior, with a natural break at the commonly anomalous europium (see below). In some geochemical literature, a group of middle REE, Nd–Tb, is also recognized.

Yttrium behavior is very similar to the HREE in the vicinity of Dy–Ho, which is why it is typically included with the other REEs in geochemical discussions. On the other hand, the geochemical behavior of scandium, especially in magmatic systems, is much more similar to the first row (ferromagnesian) transition elements, iron, vanadium, chromium, cobalt, and nickel, due to its smaller ionic radius and different coordination in mineral lattices.⁷ Because of this, many geochemists do not consider scandium as a REE, but rather as a ferromagnesian trace element. However, McLennan⁸, among others, has pointed out that in aqueous systems, scandium indeed has much more affinity for the other REE and so there is some inconsistency with REE terminology even within the geochemical literature (Figure 1).

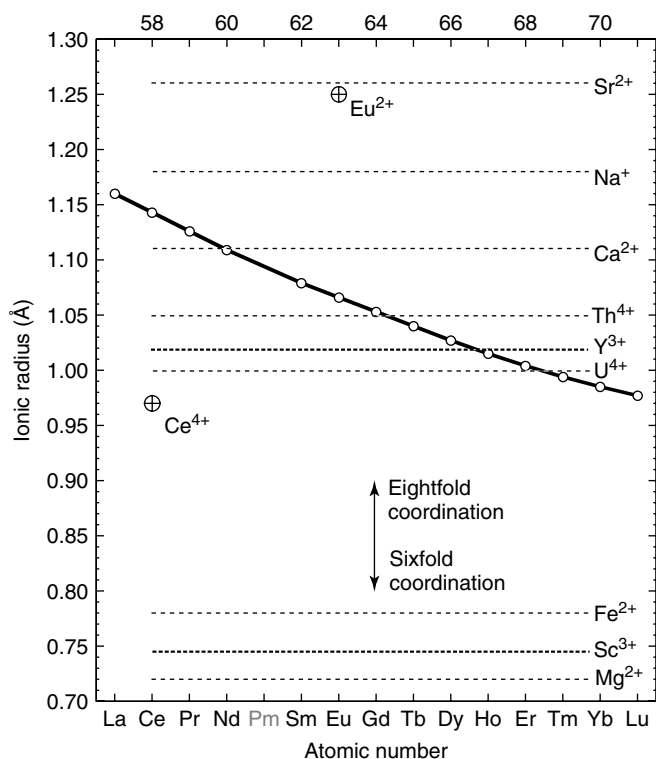


Figure 1 Plot of ionic radius versus atomic number for the trivalent lanthanide elements (La–Lu). Also shown are the ionic radii for trivalent Y and Sc, for the Eu^{2+} and Ce^{4+} , and for other selected cations. The regular decrease in the ionic radii of the trivalent lanthanides is part of the *lanthanide contraction*. Sc^{3+} is much smaller than the other rare earth elements and more similar in size to Fe^{2+} and Mg^{2+} .

The development of the lanthanide series by filling of inner 4f orbitals, which poorly shield outer electrons from the increasing nuclear charge, is the underlying cause of the remarkably coherent geochemical behavior of the group (Table 1). Among other things, this results in the trivalent state being especially stable (with two notable exceptions) and the ionic radius decreasing in a remarkably systematic manner, part of the “*lanthanide contraction*” (Figure 1; Table 1). The dominant controls on the geochemical and cosmochemical behavior of the REE are their size (ionic radius), mineral site coordination (CN), redox behavior, volatility, and complexing behavior. An additional influence, termed the *tetrad effect*, is more controversial and discussed in greater detail below. Although the lanthanides bear some chemical properties that are similar to the Group 13 elements (boron, aluminum, gallium, etc.), their geochemical and cosmochemical distributions are not significantly influenced by this.

With rare exception, REE are lithophile (“rock-loving”) in igneous systems and with the exception of Sc, are incompatible (i.e., bulk solid-melt partition coefficients, $D < 1$) with the degree of incompatibility increasing with

increasing size (and decreasing atomic number). Their ionic potentials (nominal charge/ionic radius) are ≥ 4.0 and so they are large-ion lithophile, rather than high field strength, incompatible elements. Accordingly, the lanthanides (and yttrium) tend to be concentrated in magmatic liquids and late crystallizing mineral phases. Only sodium and calcium come close in size to the REE (apart from scandium) among the major mineral-forming cations in the Earth’s crust and mantle; however, substitution for these elements (especially sodium) leads to significant charge imbalances, thus limiting any such substitutions. In aqueous alteration systems, REE have very low fluid/rock partition coefficients and thus their primary abundances are only disturbed at relatively high fluid/rock ratios under most weathering, diagenetic, hydrothermal, and metamorphic conditions. This resistance to disturbance and remobilization is another important reason why REE are considered such valuable trace elements in geochemistry and cosmochemistry.

From a cosmochemical perspective, all of the REE are refractory elements (Table 1), with relatively high 50% condensation temperatures (≥ 1356 K at 10^{-4} bar), although significant variations in volatility are present (e.g., cerium, europium, and ytterbium being less refractory than other REE). These modest differences in volatility are important for interpreting certain early formed meteorite components (minerals and inclusions) in terms of the early thermal history of the solar nebula (see below).

Under aqueous conditions, the REE exist mostly in very low concentrations as a variety of complexes, with metals (REE^{3+}), carbonate species (REECO_3^+), and bicarbonate species ($\text{REE}(\text{CO}_3)_2^-$) dominating in seawater.⁹ For a number of rare earth complexes that in nature can exist in magmatic, hydrothermal, and other fluid systems, such as fluorides, chlorides, sulfates, hydroxides, and carbonates, stability constants tend to increase with increasing temperature and decrease with increasing pressure. In general, there also tends to be an increase in stability of complexes with the heavier (smaller) REE.^{10,11} In aqueous fluids, REE concentrations tend to increase with decreasing pH.

Table 1 provides some basic data for selected REE properties of geological interest, compiled from several sources, and a thorough compilation of the full range of REE chemical and physical properties is available in Emsley.¹²

3.2 Normalization of Lanthanide Abundances

The absolute concentrations of REE in geological materials follow the Oddo–Harkins, or odd–even, effect such that even atomic number elements are of higher concentrations than their adjacent odd atomic number counterparts. Since REE concentrations and relative distributions are also highly variable among rocks and minerals, it is difficult to compare absolute abundances graphically. Accordingly, it is customary to display REE data as a plot of normalized

Table 1 Selected rare earth element properties

Symbol	Atomic number (Z)	Ground ^{12,13} state configuration	Trivalent ¹⁴ ionic radius (Å)		Atomic ^{12,13} weight	Pauling ^{12,13} electronegativity	50% Oxide ¹⁵ condensation (K at 10 ⁻⁴ bar)	
			(CN6)	(CN8)				
Lanthanum	La	57	[Xe]5 d ¹ 6s ²	1.032	1.160	138.9055	1.10	1578
Cerium	Ce	58	[Xe]4f ¹ 5d ¹ 6s ²	1.01	1.143	140.116	1.12	1478
Praseodymium	Pr	59	[Xe]4f ³ 6s ²	0.99	1.126	140.90765	1.13	1582
Neodymium	Nd	60	[Xe]4f ⁴ 6s ²	0.983	1.109	144.24	1.14	1602
Samarium	Sm	62	[Xe]4f ⁶ 6s ²	0.958	1.079	150.36	1.17	1590
Europium	Eu	63	[Xe]4f ⁷ 6s ²	0.947	1.066	151.964	—	1356
Gadolinium	Gd	64	[Xe]4f ⁷ 5d ¹ 6s ²	0.938	1.053	157.25	1.20	1659
Terbium	Tb	65	[Xe]4f ⁹ 6s ²	0.923	1.040	158.92534	—	1659
Dysprosium	Dy	66	[Xe]4f ¹⁰ 6s ²	0.912	1.027	162.500	1.22	1659
Holmium	Ho	67	[Xe]4f ¹¹ 6s ²	0.901	1.015	164.93032	1.23	1659
Erbium	Er	68	[Xe]4f ¹² 6s ²	0.890	1.004	167.259	1.24	1659
Thulium	Tm	69	[Xe]4f ¹³ 6s ²	0.880	0.994	168.93421	1.25	1659
Ytterbium	Yb	70	[Xe]4f ¹⁴ 6s ²	0.868	0.985	173.04	—	1487
Lutetium	Lu	71	[Xe]4f ¹⁴ 5d ¹ 6s ²	0.861	0.977	174.967	1.27	1659
Scandium	Sc	21	[Ar]3d ¹ 4s ²	0.745	0.870	44.955910	1.36	1659
Yttrium	Y	39	[Kr]4d ¹ 5s ²	0.900	1.019	88.90585	1.22	1659
	Eu ²⁺	—	—	1.17	1.25	—	—	—
	Ce ⁴⁺	—	—	0.87	0.97	—	—	—

Note: 50% oxide condensation temperatures are for REE oxide solid solution in pure compounds hibonite (CaAl₁₂O₁₉) ± Ca-titanate (CaTiO₃; Ca₄Ti₃O₁₀; Ca₃Ti₂O₇) ± feldspar (CaAl₂Si₂O₈).¹⁵

values (on a logarithmic scale) versus atomic number or reverse-order ionic radius (on a linear scale), termed *Coryell–Masuda plots* (Figure 2). On such diagrams, REE in rocks and minerals tend to follow smooth patterns (but with important exceptions discussed below). The two most commonly used data sets for normalization are average CI chondritic meteorites (usually on a volatile-free basis), reflecting solar and bulk Earth abundances, and average shale reflecting upper continental crust abundances (see below). Commonly used values for these two normalization sets are provided in the data tables discussed in more detail below. It should be noted that there are several different sets of chondrite values in use that differ by up to about 15% in absolute abundances (but with negligible differences in relative abundances) and so some care must be taken when comparing diagrams among different workers.

In addition to these normalization standards, it is not uncommon to normalize REE data to other compositions that are especially relevant to a specific problem. For example, in an igneous rock suite, it might be useful to normalize samples to the least petrologically evolved magmatic rock in the series. When studying weathering processes, it might be useful to normalize weathered samples to the unweathered parent rock. For authigenic minerals, insight might be gained by normalizing the mineral to the fluid from which they precipitated.

3.3 Europium and Cerium Redox Geochemistry

The existence of europium and cerium in other than trivalent states (Eu^{2+/3+}, Ce^{3+/4+}) is of considerable importance to geochemistry. Reduction of europium occurs under highly reducing conditions. Such conditions typically exist only within certain magmatic or hydrothermal environments but rarely if ever in environments found at the surface of the Earth. The ionic radius of Eu^{II} is about 17% larger than Eu^{III} and essentially identical to Sr^{II} (Figure 1). Accordingly, its substitution behavior differs greatly from the trivalent REE, resulting in anomalous REE patterns (Eu anomalies; see below). The most important geological example is that europium becomes highly concentrated in plagioclase feldspar (substituting into the calcium site). Plagioclase is only stable to about 10 kbars pressure or 40 km depth on Earth and so anomalous europium behavior in magmatic rocks is a clear sign of relatively shallow igneous partial melting or fractional crystallization processes. No example of europium reduction at surficial conditions has been convincingly documented but could potentially be present during diagenesis under highly reducing, high temperature, and alkaline conditions.¹⁶

In contrast, cerium is readily converted from Ce^{III} to Ce^{IV} under oxidizing surficial conditions. Especially notable examples are during formation of manganese oxide particles in the oceans and under certain surficial weathering conditions. Ce^{IV} is about 15% smaller than Ce^{III} and tends to form highly insoluble hydroxide complexes. These processes commonly

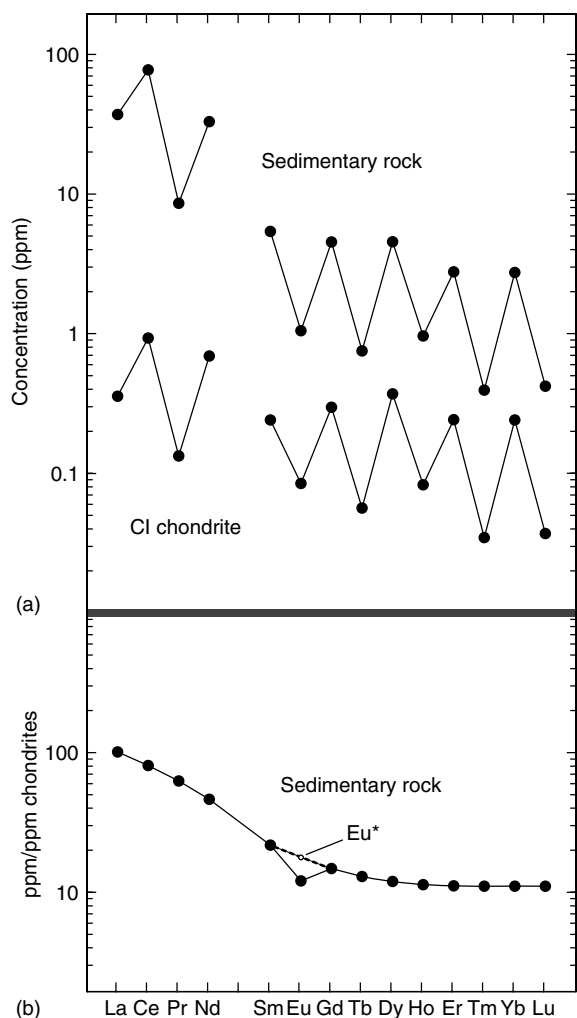


Figure 2 (a) Rare earth element abundance data for average shale and chondritic meteorites illustrating the Oddo-Harkins effect. (b) Masuda-Coryell diagram showing the average shale normalized to average chondrites. From such normalization, it is possible to readily observe the relative LREE enrichment and negative Eu anomaly in the shale. Eu^* is the expected value for Eu on a smooth chondrite-normalized pattern and used to quantify the size of the Eu anomaly. A similar formulation can be used to characterize Ce anomalies

lead to separation of cerium from the other trivalent REE, again resulting in anomalous REE patterns (Ce anomalies). The anomalous depletion of cerium in seawater (see below) as a result of manganese oxide formation is a direct reflection of such redox controls. During most continental weathering, cerium is readily oxidized to Ce^{IV} and forms highly insoluble cerium hydroxide which may be locally precipitated while other trivalent REE are more readily mobilized. The effect of this is that Ce anomalies may also occur in weathering profiles.⁸

Anomalous europium and cerium behavior can be quantified using the parameter Eu/Eu^* and Ce/Ce^* . Eu^* is

the expected value for europium for a smooth chondrite-normalized REE pattern (Figure 2), such that

$$\frac{Eu}{Eu^*} = \frac{Eu_N}{(Sm_N \times Gd_N)^{0.5}} \quad (1)$$

where the subscript “ N ” refers to the chondrite-normalized value. In the geochemical literature, arithmetic means (i.e., $(Sm_N + Gd_N)/2$) are sometimes used to calculate Eu^* but this is incorrect because REE diagrams are plotted on a logarithmic scale and can lead to serious error especially for steep chondrite-normalized REE patterns. Cerium anomalies can be similarly calculated with

$$\frac{Ce}{Ce^*} = \frac{Ce_N}{(La_N \times Pr_N)^{0.5}} \quad (2)$$

In some analytical methods, adjacent elements are not determined (e.g., gadolinium and/or praseodymium)¹⁷ and in these instances, they are estimated assuming smooth chondrite-normalized REE patterns apart from europium and cerium.

3.4 The Tetrad Effect

As the lanthanide series develops, there appears to be increased stability (manifested by a variety of observations) associated with quarter (neodymium-praseodymium), half (gadolinium), three-quarter (holmium-erbium), and completely (lutetium) filled 4f shells. Resulting anomalous behavior in REE distribution patterns has been termed the *tetrad* or *double-double* effect.¹⁸ The four tetrads are La-Ce-Pr-Nd, (Pm-)Sm-Eu-Gd, Gd-Tb-Dy-Ho, and Er-Tm-Yb-Lu. The effect was first noted in liquid/liquid partition coefficients and stability constants for organic compounds (e.g., $\log K$ of EDTA in aqueous solutions). A number of workers have also suggested that the effect can be seen in REE patterns of a wide variety of geological samples, especially those that have been influenced by aqueous interaction (e.g., seawater, marine phases) or by late-stage magmatic fluids (e.g., pegmatites). The observations that have been used to demonstrate the effect are apparent discontinuities in REE patterns at the tetrad boundaries generating either M-shaped or W-shaped REE patterns.¹⁹ Although not directly related to the phenomena, significant deviations of the Y/Ho ratio from chondritic values are also thought to commonly accompany samples with the tetrad effect.²⁰

McLennan²¹ reviewed the geochemical literature on the tetrad effect and concluded that many of the cited examples could be explained as artifacts related to a variety of factors including incomplete analyses, analytical error, inappropriate choices for normalization, and complex mixing processes that resulted in apparent discontinuities. In addition, for many sample varieties (e.g., seawater, shales), the apparent effect is observed by some laboratories but not by others. The most

compelling examples of geological environments appear to involve igneous rocks associated with late-stage magmatic fluids (e.g., pegmatites, leucogranites). In our judgment, the question of whether or not the tetrad effect is truly a significant geochemical influence will remain clouded until there is a careful and systematic interlaboratory comparison of the same samples, preferably using a variety of analytical methods.

4 MINERALOGY AND GEOLOGY OF RARE EARTH ELEMENTS

Although REE are trace elements in most rocks and minerals, there are about 200 minerals in which REE are essential structural constituents, forming necessary structural cationic components of the mineral, or are major substituting cations in the structure. Reviews of REE mineralogy, geochemistry, and geology can be found in several multi-authored books edited by Henderson²², Lipin and McKay²³, Möller *et al.*²⁴, and Jones *et al.*²⁵, the latter including a comprehensive appendix of REE minerals known

to that date. Taylor and McLennan²⁶ also provided a comprehensive review of REE geochemistry.

Cation sites in most of the common igneous rock-forming minerals, such as olivines, pyroxenes, iron-titanium-oxides, feldspars, and micas, are characterized by highly variable coordination number and charge but with overall cation site conditions that are not particularly favorable to substantial REE substitution. This, of course, is the reason why the REE are usually incompatible elements. The abundances of REE consequently tend to be low (mostly less than 100–200 times CI values) but highly varied, ranging over about five orders of magnitude, from LREE enrichment to HREE enrichment and with highly variable Eu/Eu* (Figure 3). The major influences on the REE patterns in such minerals are the mineral-melt partition coefficients (K_d), the bulk composition and REE content of the parent magma, the major element chemistry (and thus coordination of cation sites) of the mineral, and the pressure–temperature conditions at which the mineral formed.

It is this variation and the distinctive REE abundances and patterns in a wide variety of common rock-forming minerals that make the REE such useful trace elements for evaluating most igneous and metamorphic petrogenetic

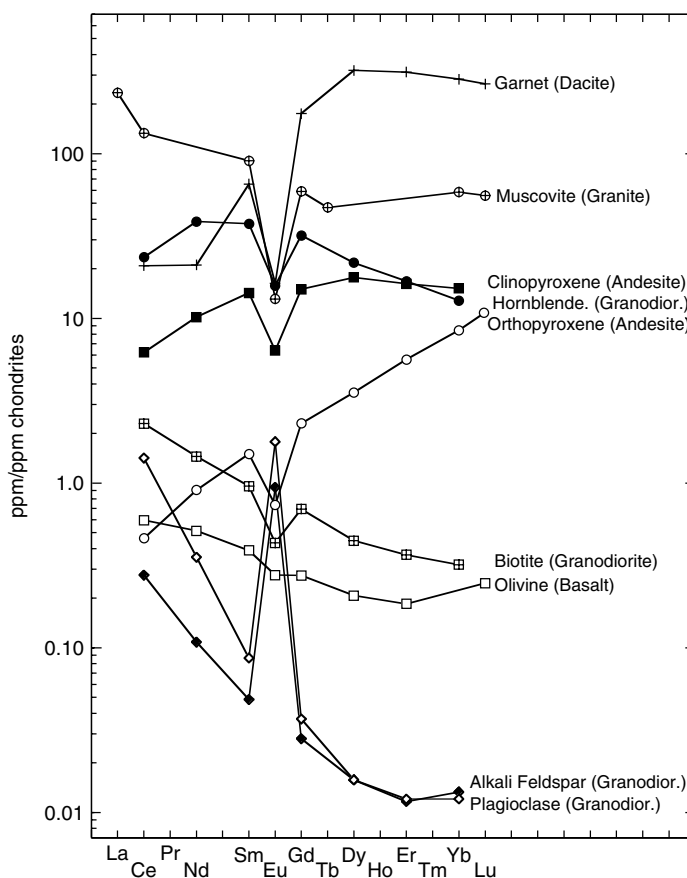


Figure 3 Chondrite-normalized REE patterns for common igneous rock-forming minerals. The igneous rock type from which the mineral was extracted is also listed. Data from compilation provided by Taylor and McLennan.²⁶ The extreme range of REE and the distinctive patterns for certain minerals is one of the reasons why REE are valuable trace elements for evaluating petrogenesis

processes. For example, Eu anomalies in magmatic rocks commonly indicate the involvement of plagioclase feldspar fractionation and HREE depletion commonly indicates a role for garnet fractionation in the history of their parent magmas. The stabilities of such minerals are sensitive to pressure, temperature, and bulk composition and thus REE patterns in rocks and minerals, coupled with an understanding of the partition coefficients, can be used to quantitatively constrain the origin and history of the magmas.

REE compounds tend to be relatively insoluble in aqueous fluids and fluid–rock partition coefficients tend to be very low during most fluid–rock interaction processes (e.g., weathering, diagenesis, hydrothermal activity). Accordingly, REE contents of most natural waters are very low, typically in the subpart per billion to subpart per trillion range. Only in high temperature, low pH hydrothermal environments do concentrations rise to near the part per million level.^{8–11} REE patterns of aqueous fluids are also highly variable, reflecting among other things the ultimate crustal or mantle sources of the dissolved REE, the nature of fluid–rock interactions (e.g., fluid/rock ratio), redox conditions and history, the nature of REE complexing ligands, and the pressure–temperature–compositional history of the fluids. In turn, minerals precipitated directly from most natural waters (e.g., carbonates, silica, evaporites, sulfides) have very low REE contents. REE are also particle-reactive under marine conditions and accordingly are readily scavenged and adsorbed onto a number of marine sedimentary particles, such as clay minerals and iron-oxides.²⁷

REE are highly electropositive (Table 1) resulting mostly in the formation of ionic compounds. REE mineral types thus include a wide variety of silicates, carbonates, oxides, phosphates, borates, halides, arsenates, sulfates, and vanadates. Among the most significant for geochemistry are lanthanite [(La,Ce,Nd)₂(CO₃)₃·8H₂O], bastnäsite [(Ce,La)(CO₃)F], allanite [(Ce,Y,Ca)₂(Al,Fe³⁺)₃(SiO₄)₃OH], and the phosphates florencite [(Ce,La)Al₃(PO₄)₂(OH)₆], monazite [(La,Ce,Th)(PO₄)], rhabdophane [(La,Ce)(PO₄)·H₂O], and xenotime [YPO₄]. Of these, the most important REE ore minerals include bastnaesite, monazite, xenotime, as well as a rare form of REE-bearing clays.²⁸

4.1 REE Ore Geology

Industrial uses of pure REE metals and compounds have expanded greatly from the early applications in incandescent gas light mantles, as polishing agents, and as glass coloring to being crucial components in a wide array modern technologies (e.g., computers, magnets, lasers, petroleum refining, alloys).^{2,3} An underlying driver of industrial development was the fundamental research carried out on the REE because of their production as fission products in the nuclear fuel cycle. The past several decades have witnessed an explosion in industrial use, much of it having considerable strategic importance (e.g., precision guidance

systems, stealth technology, night vision). Accordingly, the geological processes giving rise to ore-grade concentrations of REE are also of considerable and growing interest.

There are a number of recent reviews of the geology, geochemistry, and origin of REE ore deposits^{28–35}. The most important types of REE ore deposits include sedimentary-hosted carbonate bodies of controversial origin, igneous carbonatite bodies, heavy mineral placer sands, and several types of regolith deposit. REE patterns of major REE ores are plotted in Figure 4. Minor REE ore deposits include those related to alkaline magmatism and to early Precambrian uraniferous/auriferous quartz-pebble conglomerate paleoplacers.

By far, the largest REE ore body in the world is the Bayan Obo REE–Nb–Fe deposit hosted in Early–Middle Proterozoic carbonate rocks in north China (inner Mongolia). The geology of the deposit is complex and there is no

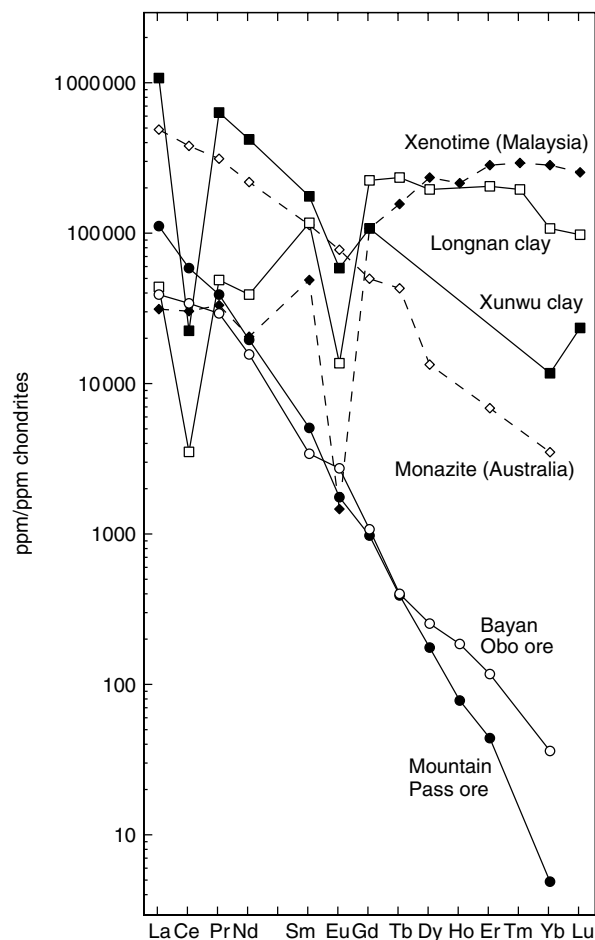


Figure 4 Chondrite-normalized REE patterns for selected REE ores from Bayan Obo and Mountain Pass; ion absorption clay ores from Longnan and Xunwu, China; and heavy mineral placer concentrates (monazite from Queensland Australia and xenotime from Malaysia)^{32,35}. Note that the ion absorption clay REE patterns are normalized to 100%.

consensus on a genetic model. The REE ore, characterized by extreme LREE enrichment and no Eu anomalies, may be related either to carbonatite magmatism and/or hydrothermal activity. The dominant REE ore minerals are bastnäsite, a readily processed REE carbonate, and monazite. Ore grades are in the range of $\sim 5\text{--}6\%$ REE₂O₃.

The Middle Proterozoic Mountain Pass LREE-Ba deposit, located in eastern California, is the second largest known economical deposit and has been mined semicontinuously since 1954 (and currently under redevelopment). The deposit is closely related to mantle-derived carbonatite magmatism with the major REE ore mineral being igneous bastnäsite, with ore grades of about 9% REE₂O₃ (other minerals in the ore include calcite, dolomite, and barite). The ore is also extremely LREE enriched but with somewhat higher HREE abundances than at Bayan Obo.

Placers represent the third most important REE ore variety that has or is being mined and occur in widely dispersed unconsolidated Neogene and Quaternary beach sands, the most important being Ti-mineral-rich beach sands on the coasts of both western and eastern Australia. REE are by-products of these deposits and the main REE ore minerals are monazite \pm xenotime. Xenotime is of special interest because unlike most other REE ore minerals that are highly LREE enriched, xenotime is enriched in the HREE (Figure 4).

The fourth variety of REE ore includes those associated with regoliths. One such deposit, exploited in China, is composed of ion absorption clays forming weathering profiles, up to ~ 10 m thick, on petrologically evolved igneous rocks such as granites. Deposits may be enriched in either LREE or HREE (and Y) and exhibit negative Eu anomalies and negative Ce anomalies. Negative Eu anomalies indicate an upper crustal source of REE and negative Ce anomalies suggest ion exchange from groundwaters depleted in cerium due to removal of insoluble Ce^{IV}-oxides during weathering. Although clays are enriched in REE, the overall grades are low ($<0.5\%$ REE₂O₃) and deposits are economical because of the ease of extraction and HREE enrichment. Another example is residual laterites that form on REE-rich rocks. The Mount Weld deposit of Western Australia, a laterite formed on a carbonatite, represents a major deposit that at the time of writing was about to go into production.³⁵

5 DISTRIBUTION OF REE IN MAJOR SOLAR SYSTEM RESERVOIRS

5.1 Solar System Abundances

The sun comprises approximately 99.87% of the mass of the solar system and its composition is the most direct estimate of the composition of the current solar system and primordial solar nebula from which the planets were derived. The REE composition of the sun can be determined

directly from spectral data for the solar atmosphere using both photospheric absorption lines and coronal emission lines. Concentration data are determined relative to some standardized concentration (typically silicon = 10^6 atoms or hydrogen = 10^{12} atoms) and one recent estimate is given in Table 2.³⁶

The second approach to estimating the composition of the solar nebula is from average Ivuna-class carbonaceous chondritic meteorites, or CI chondrites (Type 1 carbonaceous chondrites using older terminology). This class of meteorites is the most volatile rich and thus considered to be the most primitive available. CI compositions are essentially identical to spectroscopically determined solar photosphere compositions for a broad array of elements, from the most refractory to the most volatile, within analytical uncertainty. Accordingly, the REE content of average CI chondrites is taken as the best estimate of the solid fraction (i.e., “metal” fraction) of the solar nebula. Table 2 also includes an estimate of average CI chondrites recalculated to a comparable concentration scale as the solar photosphere by assuming identical silicon atomic abundances. An advantage of meteorite data for determining the composition of the solar nebula is that abundances have been determined much more precisely than are direct spectral measurements of the sun (compare uncertainties in Table 2).

5.2 Meteorites

REE distributions in meteorites and their mineralogical–lithological components provide fundamental information about the origin and early history of the solar system. Reviews of meteorite chemistry, including REE chemistry,

Table 2 Log atomic concentration of rare earth elements in the solar photosphere and CI chondrites

	Solar abundance (H = 10^{12})	CI chondrite (Si = $10^{7.51}$)
H	12.00	8.22 ± 0.04
Si	7.51 ± 0.03	7.51 ± 0.01
La	1.10 ± 0.04	1.17 ± 0.02
Ce	1.58 ± 0.04	1.58 ± 0.02
Pr	0.72 ± 0.04	0.76 ± 0.03
Nd	1.42 ± 0.04	1.45 ± 0.02
Sm	0.96 ± 0.04	0.94 ± 0.02
Eu	0.52 ± 0.04	0.51 ± 0.02
Gd	1.07 ± 0.04	1.05 ± 0.02
Tb	0.30 ± 0.10	0.32 ± 0.03
Dy	1.10 ± 0.04	1.13 ± 0.02
Ho	0.48 ± 0.11	0.47 ± 0.03
Er	0.92 ± 0.05	0.92 ± 0.02
Tm	0.10 ± 0.04	0.12 ± 0.03
Yb	0.84 ± 0.11	0.92 ± 0.02
Lu	0.10 ± 0.09	0.09 ± 0.02
Sc	3.15 ± 0.04	3.05 ± 0.02
Y	2.21 ± 0.05	2.17 ± 0.04

can be found in Brearley and Jones³⁷, Mittlefehldt *et al.*³⁸, and McSween and Huss³⁹.

REE patterns in bulk carbonaceous chondrites are fairly uniform, parallel to CI, and show no dependence on volatility (e.g., no Eu or Yb anomalies). This uniformity also applies to the ordinary (H, L, LL classes) and enstatite (EL, EH classes) chondrite classes that show significant loss of their moderately and highly volatile elements (e.g., potassium, lead) and/or variations in their metal/silicate ratios. Accordingly, REE abundances in chondritic meteorites indicate no substantial cosmochemical fractionation (i.e., volatile related; redox related) during their formation in the early stages of solar system evolution and indicate broad homogeneity in the solar nebula.

On the other hand, millimeter to centimeter scale calcium–aluminum refractory inclusions (CAI) and individual refractory mineral inclusions (e.g., hibonite (CaAl_2O_9) and perovskite) from the Allende and Murchison carbonaceous chondrites provide evidence for local heterogeneity in the early solar nebula related to very high-temperature processes.^{40,41} CAIs have been radiometrically dated as the oldest known objects in the solar system (4.567 billion years old) and exhibit highly variable REE patterns with variable Eu and Yb anomalies, in the case of CAIs, and Ce, Eu, and Yb anomalies in the case of hibonite grains (Figure 5). Such anomalies cannot be related to magmatic processes but instead are due to complex evaporation–condensation processes that fractionated the least refractory cerium, europium, and ytterbium from the other more refractory REE (Table 1). This veritable “zoo” of REE patterns calls for very high local temperatures, very complex histories of evaporation and condensation, and local compositional heterogeneity.

Silicate-bearing differentiated meteorites from the asteroid belt, including achondrites and stony-iron meteorites, are thought to represent fragments from asteroidal parent bodies that were melted very early in the history of the solar system and differentiated into core, mantle, and crust. REE data from these materials show significant variations, compared to chondrites, which reflect the magmatic histories of their parent bodies. For example, the howardite–eucrite–diogenite (HED) meteorites appear to be petrologically interrelated and probably are derived from the large asteroid 4-Vesta. REE patterns of the basaltic eucrites display variable positive and negative Eu anomalies that can be related to partial melting histories within Vesta.

Meteorites that do not come from the asteroid belt include the so-called SNC meteorites (for shergottites–nakhilites–chassignites) derived from Mars and the lunar meteorites. These were ejected from the planetary surfaces during impact processes and their REE compositions are highly variable, reflecting the magmatic evolution of these planetary bodies (see below).

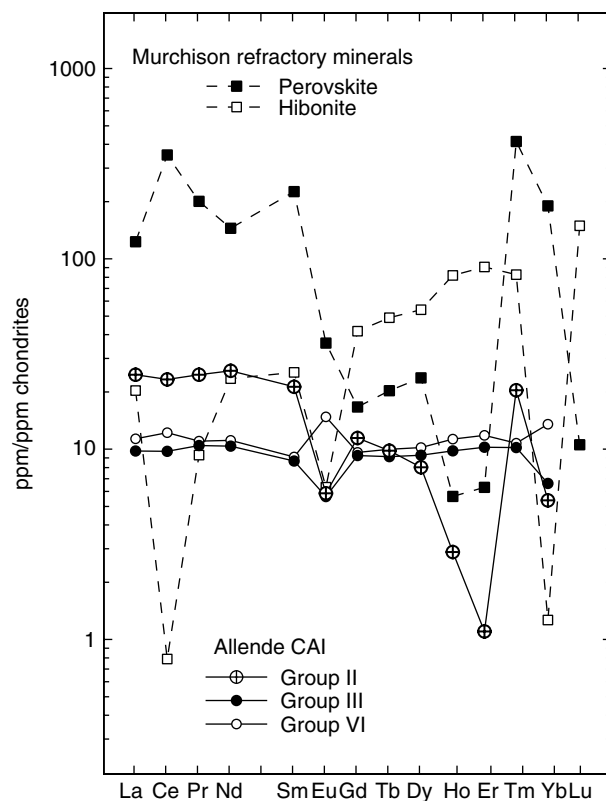


Figure 5 Chondrite-normalized REE patterns for selected calcium–aluminum inclusions (CAI) from the Allende carbonaceous chondrite and refractory mineral grains (perovskite, hibonite) from the Murchison carbonaceous chondrite.^{40,41} The highly irregular REE patterns, including anomalies for the least refractory Ce, Eu, and Yb, are indicative of localized very high temperatures leading to complex REE evaporation/condensation processes

5.3 Planetary Compositions

As refractory lithophile elements, the REE play an important role in constraining the overall composition and history of the silicate fraction of planets, which for the terrestrial planets is also termed their *primitive mantle* (equivalent to the present-day crust plus mantle). Since there is no evidence for significant planetary-scale fractionation of refractory elements during the assembly and differentiation of planetary bodies, it is widely accepted that the primitive mantles of terrestrial planets and moon possess chondritic proportions of the REE. As such, the absolute concentrations of REE (and other refractory elements) in primitive mantles provide an important constraint on the proportions of volatile elements to refractory elements and on the oxidation state (i.e., metal/silicate ratio) of the body. To date, the only major planetary bodies for which REE data are directly available are the Earth, Moon, and Mars, and Taylor and McLennan⁴² recently reviewed these data.

There is an enormous body of knowledge upon which to base estimates of the composition of the primitive mantle of

Table 3 Estimates of REE concentrations in the primitive mantles of Earth, Mars, and Moon and crusts of Mars and Moon⁴²

	Average CI chondrite	Average volatile-free CI chondrite	Earth primitive mantle	Mars primitive mantle	Mars crust mantle	Moon primitive mantle	Moon highland crust
La	0.245	0.367	0.546	0.480	5.5	1.10	5.3
Ce	0.638	0.957	1.423	1.250	13.9	2.87	13
Pr	0.0964	0.137	0.215	0.180	1.9	0.411	1.8
Nd	0.474	0.711	1.057	0.930	9.4	2.13	7.4
Sm	0.154	0.231	0.343	0.300	2.7	0.69	2.0
Eu	0.058	0.087	0.129	0.114	0.95	0.26	1.0
Gd	0.204	0.306	0.454	0.400	3.1	0.92	2.3
Tb	0.0375	0.058	0.084	0.076	0.55	0.17	0.35
Dy	0.254	0.381	0.566	0.500	3.4	1.14	2.3
Ho	0.0567	0.0851	0.126	0.110	0.70	0.255	0.53
Er	0.166	0.249	0.370	0.325	1.9	0.75	1.51
Tm	0.0256	0.0356	0.057	0.047	0.25	0.11	0.22
Yb	0.165	0.248	0.368	0.325	1.7	0.74	1.4
Lu	0.0254	0.0381	0.057	0.050	0.26	0.11	0.21
Sc	5.90	8.64	13.0	11.3	-	19	5
Y	1.56	2.25	3.48	2.7	18	6.3	13.4

Concentrations in parts per million ($\mu\text{g g}^{-1}$).

the Earth. There are basically two approaches: (i) those based on the composition of xenoliths and high-degree partial melts from the upper mantle, and (ii) those based on fundamental cosmochemical principles. In practice, both lines of evidence are employed and models differ mostly in the relative weight given to each. As discussed above, it is generally assumed that refractory elements are not fractionated from each other in the primitive mantles of planetary bodies. Thus, for the Earth, the REE abundances can be derived by assuming that ratios such as REE/Ca and REE/Al are in chondritic proportions. In turn, absolute abundances of refractory elements depend on the diluting effects of (i) amount of relatively volatile elements in the primitive mantle and (ii) oxidation state of the planet, which controls the proportion of iron partitioned into the metal core and silicate primitive mantle. Table 3 lists estimates for the REE contents of the primitive mantles of Earth, Mars, and the Moon, and chondrite-normalized plots are given in Figure 6.

The terrestrial planets and other large silicate-rich planetary bodies (e.g., large asteroids, moons) typically are differentiated into metal cores, silicate mantles, and incompatible element-enriched silicate crusts. The mechanisms, scales, and timing of this process are extremely variable.⁴² For REE, crust–mantle differentiation is the most important process in controlling abundances and distributions; REE are essentially excluded from planetary metal cores due to their lithophile character. In Table 3 and Figure 6, estimates of the REE distributions in planetary crusts (Earth's continental crust, lunar highland crust, Martian crust) are also given. In the following sections, we discuss the REE content of the Earth's crust in much greater detail.

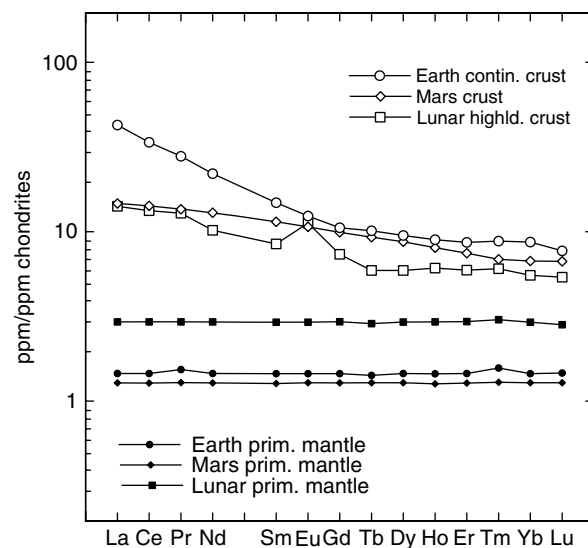


Figure 6 Chondrite-normalized REE patterns of the primitive mantles and crusts of Earth, Mars, and the Moon. For the Earth, the continental crust is shown; for the Moon, the highland crust is shown; and for Mars, the bulk crust is shown

6 DISTRIBUTION OF REE IN TERRESTRIAL RESERVOIRS

The major geochemical reservoirs of the Earth that are currently in existence—inner and outer core, upper and lower mantle, upper and lower continental crust, oceanic crust, sedimentary shell, oceans, and atmosphere—were established early in the planet's history. On the other hand, the sizes and compositions of these reservoirs have changed over