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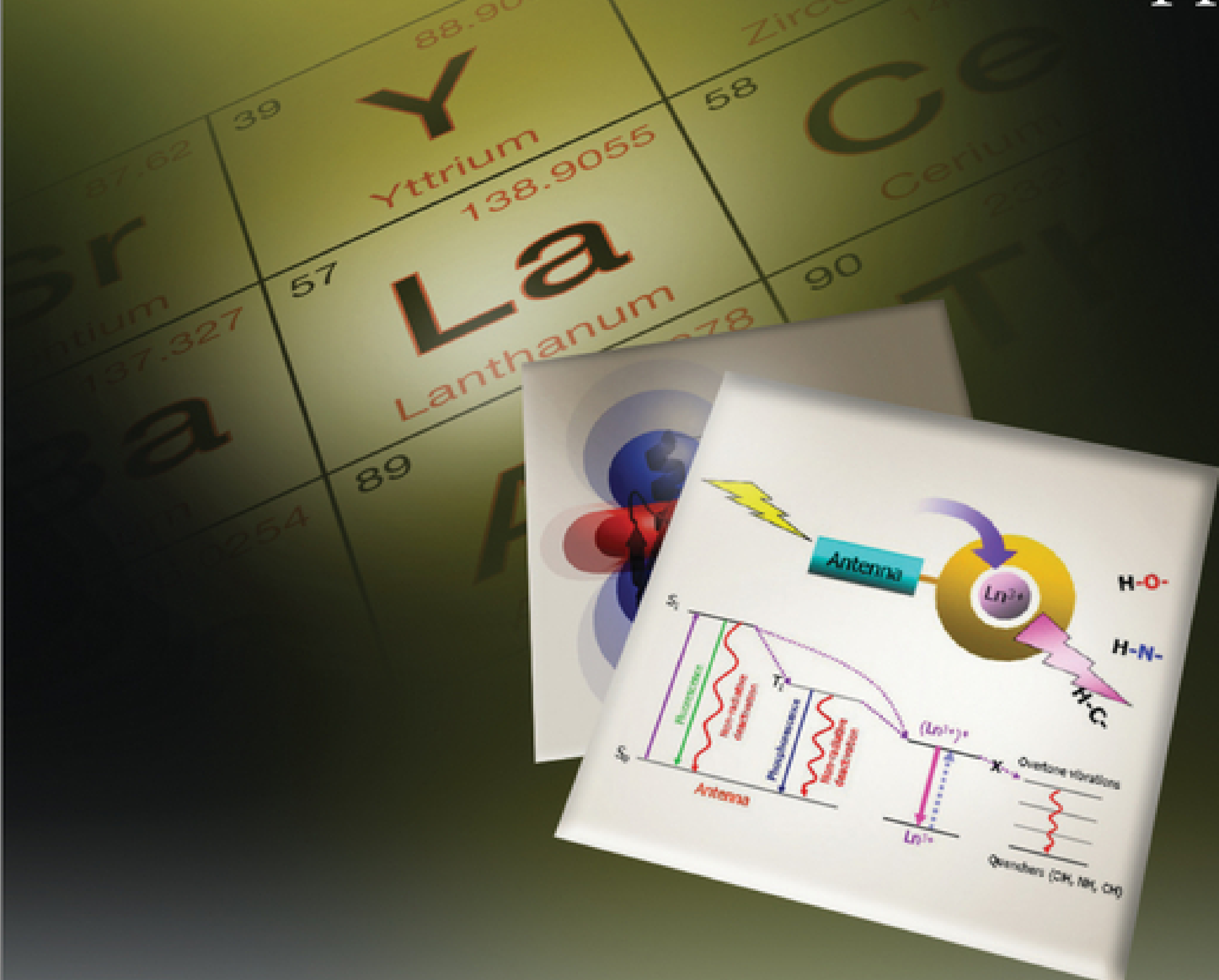
The Rare Earth Elements
Fundamentals and Applications



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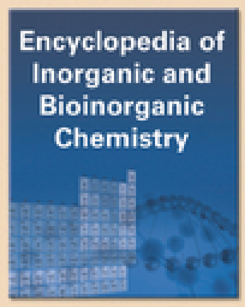

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THE RARE EARTH ELEMENTS:

Fundamentals and Applications

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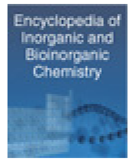

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The Encyclopedia of Inorganic and Bioinorganic Chemistry (EIBC) was created as an online product in 2012 as a merger of the Encyclopedia of Inorganic Chemistry (which published online in 2006) and the Handbook of Metalloproteins (which published online in 2006). The resulting combination proves to be the defining reference work in the field of inorganic and bioinorganic chemistry. The online edition is regularly updated and expanded. For information see:

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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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Department of Chemistry

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.

David A. Atwood
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May 2012

THE RARE EARTH ELEMENTS: Fundamentals and Applications

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., ^{147}Sm–^{143}Nd, ^{146}Sm–^{142}Nd, ^{176}Lu–^{176}Hf, ^{138}La–^{138}Ce) 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