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The Rare Earth Elements

An Introduction

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Preface

This book was written as a summary of my long-standing interest in rare earth elements, which had started already when I was a master student at Utrecht University in the 1980s. Having begun seriously to tackle the topic early in 2009, it appeared that, during the so-called rare earth crisis from 2009 to approximately 2013, I was considered a kind of 'sole expert' in the Netherlands on rare earth element resources. This led me to being asked to give numerous presentations.

As a result of these many presentations, I realised that there was little or no information on the rare earth elements for the well-educated non-expert. So, in June 2014, after having given the umpteenth presentation on rare earth elements for an audience of members of the Groningen Department of the Royal Dutch Chemical Society (KNCV), I started with the preparations for writing this book.

This book is thus intended for the well-educated but non-expert reader, from any natural science discipline. This also explains the numerous footnotes scattered throughout the book, which are intended to elucidate the used terminology, or to supply short background information.

For the opportunity to write this book, I first of all would like to thank Dr. Mike Buxton, Head of the Resource Engineering Section, Delft University of Technology, who earnestly suggested me to write this work and allowed me to write it as part of my duties at Delft University. He also mentioned the importance of the South African Pilanesberg and Steenkampskraal deposits and supplied me with several papers and reports from the literature on these and other deposits.

Furthermore, this book could never have been written without the help and support of the following persons, companies, and institutions, which are listed here in alphabetical order:

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Delft Jack Voncken
October 2015

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Chapter 1
The Rare Earth Elements—A Special Group of Metals

Abstract This chapter explains what the rare earth elements are, where and when they were discovered, and by whom. The name of each element is explained (as the elemental names are rather exotic), the misleading name for these metals, which suggests that they are rare (which they are not), is clarified, and the fact that they are not earth metals is established. The alkaline earth metals constitute group IIA in the periodic system, consisting of Be, Mg, Ca, Sr, Ba, and Ra; the rare earth elements are transition metals (group IIIB).

1.1 Introduction

Over the last few years, more and more people have become aware of a rather special group of metals: the rare earth elements. Many people have never heard of them, or probably just know them as "the upper one of these two rows of elements beneath the main body of the Periodic System of the Elements". Indeed, these metals, with a surprisingly large amount of applications, were rather obscure to the general public until 2009.

In 2009, China, which had almost a monopoly on the production of these elements (97 % of the world production), changed its position towards the world-wide rare earth market. China introduced production quotas, export quotas and export taxes, enforced environmental legislation, and granted no new rare earth mining licenses (Geschneider 2011). This caused world-wide anxiety among manufacturers of high tech equipment, because many of today's common (mostly) high-tech applications are not feasible without rare earth elements. Notable examples are hard-disk drives, smart phones, flat-screen televisions and monitors, rechargeable batteries (household and automotive) and tiny earphones. Others are lasers, strong permanent magnets for electrical generators, glass-polishing powders, and energy-saving lamps. This period, starting in 2009 and known as the "Rare Earth Crisis," made many people around the world aware of this peculiar group of elements.

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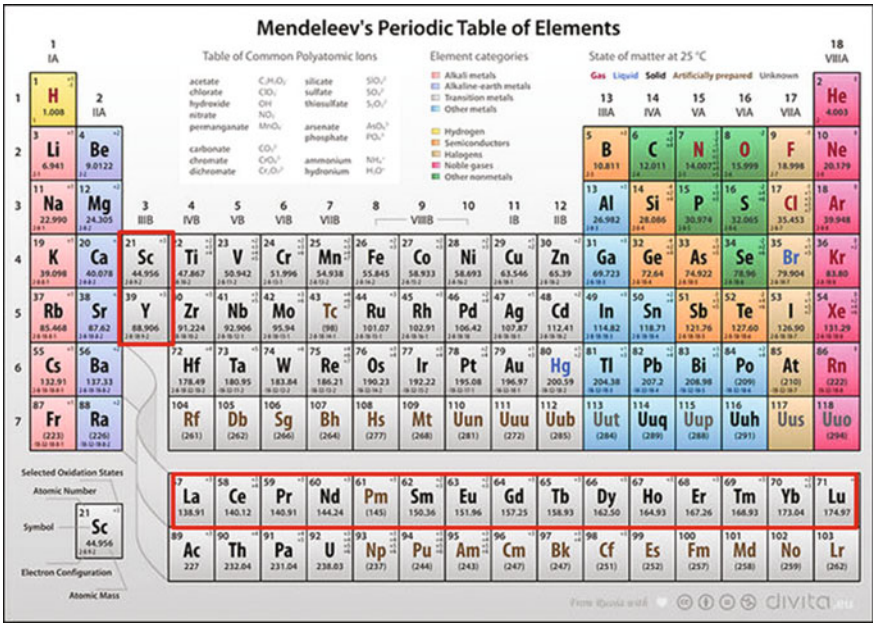

Fig. 1.1 The Periodic System of the Elements. *Reference* http://www.redbubble.com/people/seifip/works/5309681-mendeleevs-periodic-table-of-elements?p=poster. The REE including Sc and Y, are outlined in *red*

The rare earth elements are known under several names: rare earth metals, rare earths, or simply REE. They are a group of 17 strongly related heavy elements that comprise Sc, Y, and the Lanthanide Group. In Fig. 1.1, they are shown in the Periodic System of the Elements, outlined in red. The lanthanides should be positioned between the elements barium (Ba) and hafnium (Hf).

The discovery of the rare earth elements started at the end of the 18th century. The first element to be discovered was Yttrium, by Finnish chemist and mineralogist Johan Gadolin (Gadolin 1794, 1796; Weeks 1968; Gupta and Krishnamurthy 2005). See Fig. 1.2 for a portrait of Gadolin. By the end of the 19th century, all but two of the rare earth elements had been discovered. Lutetium was discovered in 1907, and the last one (promethium) only after the discovery of nuclear reactions. Promethium was identified in 1947 (Marinsky et al. 1947).

The rare earth elements are the elements ^{21}*scandium (Sc)*, ^{39}*yttrium (Y)*, ^{57}*lanthanum (La)*, ^{58}*cerium (Ce)*, ^{59}*praseodymium (Pr)*, ^{60}*neodymium (Nd)*, ^{61}*promethium (Pm)*, ^{62}*samarium (Sm)*, ^{63}*europium (Eu)*, ^{64}*gadolinium (Gd)*, ^{65}*terbium (Tb)*, ^{66}*dysprosium (Dy)*, ^{67}*holmium (Ho)*, ^{68}*erbium (Er)*, ^{69}*thulium (Tm)*, ^{70}*ytterbium (Yb)*, *and* ^{71}*lutetium (Lu).*

The rather exotic names of these elements (compared to, for instance, lead and iron) will be explained later.

Fig. 1.2 Johann Gadolin. *Image Source* Wikipedia (2015) Johann Gadolin. *Reference* Dean and Dean (1996)

1.2 Atomic Structure

In the lanthanides (the elements La–Lu) the *f-orbitals*, which have 7 sub-orbitals, are filled. Each suborbital holds two electrons. As a result of this, there are 15 possibilities for filling the *f*-orbitals, giving rise to 15 lanthanide elements. These elements have closely related properties.

The lanthanides are all trivalent (3+), with the exception of cerium (which also forms 4+ ions), and europium, ytterbium, and samarium, which also will form 2+ ions.

The elements scandium and yttrium, which are also considered to belong to the rare earth elements (because of their similar chemical behaviour) also have a 3+ oxidation state. The atomic structure of the REE is further discussed in Chap. 3 (Physical and Chemical Properties of the Rare Earths).

1.3 Radioactivity

Of the rare earth elements, only one element is radioactive and has no stable isotopes. All other of these elements have stable isotopes, although for several elements, the isotopes have limited stability, but a very long half-life, so they may be considered stable. The radioactive element without a stable isotope is the element promethium (Pm). Promethium does not occur as a free element on Earth, whether as a metal or in compounds. It is synthetically manufactured in nuclear reactors, as it has practical applications. The radioactivity of promethium is further explained in Chap. 3.