

Chapter 2

Rare Earth Elements: What and Where They Are

2.1 Definitions

REE are often misunderstood, beginning from the grouping of the relevant elements to the etymological misconception, that REE are rare or the fact that REE are ‘more abundant than gold’. Thus REE can get the impetus of being very abundant, which is only part of the truth. As well the allegation “The term rare earth is actually a misnomer” [1, p. 3] shows a cursory view of these metals. This view is for most purposes probably good enough, like the need for a 5-min-overview of the REE. The problem here lies in a possible wrong perception which finally gets to a seemingly hard fact because ‘everybody says so’. In order to get a scientific plausible picture, several definitions are given at the beginning.

2.1.1 *The Group of the REE*

The Rare Earth Elements (REE), also simply called Rare Earths (RE) or Rare Earth Metals (REM), are a group of 17 elements—according to the International Union of Pure and Applied Chemistry (IUPAC) [2, p. 51]. The 17 REE therefore consist of the elements scandium (Sc), yttrium (Y) and the 15 so called lanthanoids (Ln) which are the elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Th), ytterbium (Yb) and lutetium (Lu) [2]. Mortimer and Müller [22] in their chemistry and Meschede [3] in the physics both group the lanthanoids and rare earths synonymously and count 14 elements from Cerium to lutetium, i.e. without lanthanum itself [4, 3, p. 849]. Often the name lanthanides is used instead of lanthanoids. The ending—id however indicates a certain chemical structure like a sulphide whereas the ending—oid means that something is similar, looks or behaves the like. So the word lanthanoids would be the correct one to use as the REE are not derivations

from lanthanum but they are similar to lanthanum. Even though that would preclude lanthanum itself from the group, the inclusion of lanthanum has become common use [2].

2.1.2 The Terms ‘Rare’ and ‘Earth’

The name ‘Rare Earths’ is misleading as the name itself implies an earthen material which is not ubiquitous. To start with the easy part, the word ‘earth’ was a common denomination for an oxidic material, usually a metal oxide, i.e. a compound of an element with oxygen. In the German language there is another cause for error as the German word for earth, ‘Erden’, can be misunderstood with the expression ‘Steine und Erden’, which in the German language stands for materials from pit and quarry industry. Of course the ‘Steine und Erden’ have nothing to do with RE.

The more difficult part is the adjective ‘rare’. Reiners [5] suggests that ‘rare’ has more of an etymological background, as ‘rare’ was used from the late 15th century onwards in the sense of something strange, extraordinary, astonishing [5]. REE are not per se rare and in abundance lists they range somewhere from the second half to the beginning of the last third compared to the other elements. This abundance topic is a research field of the geochemistry where Frank W. Clarke, as chief chemist of the United States Geological Survey founded in 1884, published a first estimate of elemental abundance in 1889. Another major protagonist is V. M. Goldschmidt who decisively invented methods to determine the abundance of elements in minerals at around the 1920s. More details about the initial phases of geochemistry and abundance tables are elaborated by Mason et al. [14]. Initially earth samples were taken and abundances derived thereof. Later, meteorite data were taken as well to determine abundances of the stellar, solar and earth elemental abundances [6–8]. Today there are numerous abundance tables available with usually different approaches, assumptions and geographical sample areas, so that no uniform list can be presented. Rudnick and Gao [9] give a fundamental insight into the composition of the continental crust and the research in the field which they call ‘myriad studies on continental crust composition’ [9]. They come up with a new suggestion for the bulk composition differentiated in an upper, middle, lower and total crust value. Table 2.1 shows some selected elements and the proposed composition of Rudnick and Gao [9]. As a comparison to illustrate the differences also the abundance estimates of Binder [10] and Allègre et al. [6] have been added.

Table 2.1 shows that there is no uniform estimate: Rudnick and Gao [9] put the least abundant REE, lutetium and thulium, behind platinum and gold. Binder [10] lists lutetium and thulium before silver, gold and platinum, i.e. more abundant whereas in Allègre et al. [6] they again range behind, i.e. less abundant than gold and platinum. So the abundance tables are more or less of theoretical value. The basic data Binder [10] is using in his encyclopedia is not known. Allègre et al. [6]

Table 2.1 Elemental composition of the Earth

Composition of the Earth-comparison of different authors' data and levels of detail						
Element	Upper crust	Middle crust	Lower crust	Total crust	Composition of the Earth's crust	Bulk composition of the Earth
	Rudnick and Gao [9, p. 53f] ($\mu\text{g g}^{-1}$)				Binder [10, p.776f]	Allegre et al. ([6], p. 61)
	(\approx ppm)					
Sc	14	19	31	21.9	20 ppm	10.1 ± 2 ppm
Y	21	20	16	19	31.5 ppm	2.4 ± 0.2 ppm
Cu	28	26	26	27	68 ppm	64.7 ± 5 ppm
La	31	24	8	20	35 ppm	415 ± 10 ppb
Ce	63	53	20	43	68 ppm	1088 ± 20 ppb
Pr	7.1	5.8	2.4	4.9	9.5 ppm	165 ± 5 ppb
Nd	27	25	11	20	40 ppm	814 ± 10 ppb
Sm	4.7	4.6	2.8	3.9	7.5 ppm	259 ± 3 ppb
Dy	3.9	3.8	3.1	3.6	6.2 ppm	424 ± 10 ppb
Tb	0.7	0.7	0.48	0.6	1.2 ppm	66.6 ± 5 ppb
Lu	0.31	0.4	0.25	0.3	0.81 ppm	42.5 ± 2 ppb
Pt	0.5	0.85	2.7	1.5	0.004 ppm	1562 ± 40 ppb
Au	1.5	0.66	1.6	1.3	0.0041 ppm	102 ± 20 ppb

REE marked bold italic

base the determination of abundance tables or the bulk chemical composition of the earth on the comparison of terrestrial samples with meteorite data. As earth samples can only be gained from the very outer parts of the earths' crust, one way to attain knowledge is to use meteorite data which is assumed to constitute the original material composition shortly after the big bang. So the idea is to infer from these chondrites to the earths composition. Research showed that there is a high similarity of elemental composition of a special type of chondrites, the so called CI chondrites, and the earth's composition gained by terrestrial samples.

Numbers for the geosphere are usually given in percent of mass (%); data for the earths' crust is given in parts per million (ppm), respectively grams per metric ton (g/t) [10]. The numbers allow the calculation of theoretical quantitative data but they do not imply that more abundant elements are more easily exploitable as less abundant ones. As not all elements occur in pure or elemental form but usually as one constituent amongst many others within a mineral, it depends on the grade if an element mining or extraction is feasible. Skinner [11] introduced the term 'mineralogical barrier' by which he distinguishes abundant elements where mining is feasible. The barrier also determines the required grade for scarce elements to allow economic exploitation [11]. The Clarke-value is another determination of necessary enrichment grade for economic mining (e.g. [12]). As here also economic mining is addressed, of course this value is dependent on available technical options and commodity prices. So the value actually has to be amended as soon as prices or technology and thus extraction cost change.

The geochemistry tries to determine the petrogenetic processes which led to the minerals that can be found today [13, 14]. Usually endogen processes are assumed when in 2011 Willbold et al. [15] determined that ‘iron-loving’ metals like gold are surprisingly abundant in the earths’ crust. So they came up with a new probable explanation that a terminal bombardment of meteorites after the earths’ core formation around 4 billion years ago contributed to the earths’ elemental composition. The actual composition respectively abundance is even more difficult to determine and as such the direct economic value of abundance tables is questionable.

In this context another question arises when the theoretical abundance data are compared with common mineral compositions. It could be asked: where are all the ‘missing’ REE? The abundance tables show a higher or near similar abundance for neodymium than for lanthanum: 35 ppm (La) and 40 ppm (Nd) [10], 32 ppm (La) and 38 ppm (Nd) [16], 415 ppb (La) and 814 ppb (Nd) ([6] or $31 \mu\text{g g}^{-1}$ (La) and $27 \mu\text{g g}^{-1}$ (Nd) [9]). This means that in general there should be more neodymium available in the earths’ crust than lanthanum. This is applicable for the composition of the earth as such, but similar relationships are known for the composition within the geosphere alone [10]. However, looking at the major REE minerals like e.g. the bastnaesite of the Bayan Obo type (explanation in following chapter) the concentration is given as approximately 25 % for La_2O_3 and 17 % for Nd_2O_3 [17] or 33.27 % La_2O_3 and 12.02 % for Nd_2O_3 [18, p. 837]. For monazite, the next important REE mineral there are similar numbers given [18, p. 837]. So where is the missing neodymium? There most probably is no undetected new mineral which hosts all the Nd, moreover the chemical characteristics of the REE and their behavior in melts lead to a better incorporation of lanthanum into mineral genesis than neodymium. Due to a higher ionic radius lanthanum is more readily built into rocks than neodymium. As a consequence neodymium remains more dispersed in surrounding rocks and does not aggregate enough. More substantial information is given by Stosch [19].

Eventually, as a conclusion it has to be noted that the mere position in an abundance table does not at all reflect any actual proof of an economic exploitation. So the message that REE are more abundant in the earth’s crust than gold or platinum is of no economic use and rather misleading information.

2.1.3 Light, Medium and Heavy REE

Next, the REE are usually attributed to the groups of the light REE (LREE), the heavy REE (HREE) and sometimes to the medium or middle REE (MREE). The grouping to these three classes is not consistent among different authors, as can be seen in Table 2.2. The only reasonable *argument* or the grouping of the REE into ceric and yttric is given by Röhr [20] and the USGS [21]. They argue that the electron configuration is the basis for the distinction of the two groups.

Table 2.2 Rare Earth elements—overview of selected characteristics

Rare Earth Elements - selected characteristics, chemical data and the grouping into LREE, MREE and HREE																	
Atomic number	21	39	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Element	Sc ⁽¹⁾	Y ⁽¹⁾	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Orbitals ⁽¹⁾	3d ¹ 4s ²	4d ¹ 5s ²	5d ¹ 6s ²	4f ⁶ 6s ²	4f ⁶ 6s ²	4f ⁷ 5d ¹ 6s ²	4f ⁶ 6s ²	4f ⁷ 6s ²	4f ¹⁴ 6s ²	4f ¹⁴ 5d ¹ 6s ²							
Oxidation states ⁽¹⁾	+3	+3	+3	+3	+3	+3	+3	+3	+2	+3	+3	+3	+3	+3	+3	+2	+3
Color ⁽¹⁾			no color	no color	yellow	green	yellow	pink	yellow	no color	nearly no color	yellow	green	yellow	pink	green	no color
Atomic radius [pm] ⁽¹⁾	162	180	187	182	182	181	181	180	204	179	178	177	176	175	174	193	174
Ionic radius [pm] ⁽¹⁾			103	101	99	98	97	96	95	94	92	91	90	89	88	87	86
Atomic mass [u] ⁽¹⁾	45.0	88.9	138.9	140.1	140.9	144.2	144.9	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0
Mass in geosphere [kg] ⁽²⁾	5 · 10 ⁻⁴	0.003	0.002	0.004	5 · 10 ⁻⁴	0.002	10 ⁻⁶	6 · 10 ⁻⁴	10 ⁻⁵	6 · 10 ⁻⁴	9 · 10 ⁻⁵	4.2 · 10 ⁻⁴	10 ⁻⁴	2 · 10 ⁻⁴	2 · 10 ⁻⁴	3 · 10 ⁻⁴	7 · 10 ⁻⁵
Boiling point [K] ⁽²⁾	3104	3611	3730	3699	3785	3341	~3000	2064	1870	3539	3396	2835	2968	3136	2220	1466	3668
Melting Point [K] ⁽²⁾	1814	1795	1194	1072	1204	1294	1441	1350	1095	1586	1629	1685	1747	1802	1818	1097	1936
Density [kg/m ³ at 293K] ⁽²⁾	2989	4469	6145	8240	6773	7007	7220	7520	5243	7900	8229	8550	8795	9066	9321	6965	9840
	[273K]		[298K]							[298K]			[298K]	[298K]			[298K]
Classification of metals	Heavy metals (Density > 5000 kg/m ³)																
Binder [10], p. 342; USGS 2011 b (Cordier)	Ytterbiden (yttric earths), HREE																
Rohr [20]	Ytterbiden (yttric earths), HREE																
Cesbron [87], p. 5; ROMPP Online [23] ⁽⁴⁾	Light Rare Earth Elements (LREE), Cerium group																
Pohl [29], p. 212	LREE																
Kingsnorth [89], p. 4	LREE																
Stoisch [19], p. 2	LREE																
Chen [44]	HREE																
Notes and data sources:	(1) Mortimer 2001, p. 501f (2) Emsley [16], p. 233 (3) Merck 2007. Data for Sc and Y have been extracted from Merck PSE (4) keyword 'Seltenerdmetalle' blank cells - no data was available or no information given The overview shows - next to some chemical data - the persisting discrepancies in grouping of the REE into the light, medium and heavy fractions.																

The electron configurations f^0 (all f-instances are unoccupied), f^7 (half of the f-instances are occupied) and f^{14} (all f-instances are occupied) are considered more stable than the other configurations. So these more stable instances can act as borders for the groups such as to group the elements cerium—gadolinium to the ceritic earths or light rare earth elements (LREE) and terbium—lutetium to the yttritic earths or heavy rare earth elements (HREE). A reason for not attributing lanthanum to the LREE is that lanthanum is no f-element, so it does not fit to the LREE-nomenclature. Cerium however can and should be regarded as a 1f-state due to its position within the periodic system of elements and the reactivity of cerium (personal information from Röhr [20]). Stosch [19] gives an explanation for counting yttrium to the HREE. Yttrium stands just above the other REE within the periodic system, so that this gives a hint for similar characteristics within these elements. This is of course true for all REE so that another argument seems more plausible: indeed the ionic radius of yttrium is nearly the same as for dysprosium or holmium and the chemical behavior of yttrium is very similar to holmium so that they can be grouped together into the HREE.

2.1.4 Rare Earths, Rare Elements and Rare Metals

Another misconception results from the similar names: rare earth, rare metals and rare elements. They are not the same and cannot be used synonymously, even though that happens quite often. The REE themselves have been explained already. The group of the *rare metals* does not have a commonly accepted list of metals; instead the arrays differ from author to author. And, over time the allocations of elements to the list change frequently, so that an inherent temporal aspect has to be attributed. Skinner [11] mentioned that the 12 most abundant elements (O, Si, Al, Fe, Ca, Mg, Na, K, Ti, H, Mn, P) in the continental crust account for 99.23 % of the mass of the crust. He therefore introduced all metals with a share of less than 0.1 % on the continental crust as geochemically *scarce* metals [11, p. 563f]. Scarce is often used as a synonym for *rare* thus the definition of rare metals is sometimes derived from Skinner as being the metals with an abundance share of less than the 0.1 %. The group of rare elements now generally addresses all elements, not only metals. Within this nomenclature the rare earths consequently can be considered as a subset of the rare metals which again can be seen as a subset of the group of the rare elements.

2.2 Chemical and Physical Properties

Details about the special chemical and physical properties are explained in appropriate scientific encyclopedias and standard works about chemistry and physics like Mortimer and Müller [22], RÖMPP Online [23], Meschede [3] and

many more. The three given books build the basis for this short chapter and will not be cited within the chapter any further. As these books give a very thorough insight into the topic only a brief description is given here about some characteristics which are deemed important to understand the complex creation, extraction and separation processes of the REE.

In the periodic system of the elements the REE are transition metals and belong to the third subgroup, the scandium-group, together with scandium, yttrium and the group of the radioactive actinides. The lanthanoids demonstrate special electron configurations on the atomic level. The atomic cores are surrounded by electrons on several orbitals and with increasing atomic number protons, neutrons and electrons are gained. The electrons usually attach to the outer orbitals. For the lanthanoids however, not the outer shell is filled but a deeper lying orbital accommodates the new electron(s): the 4f-orbital. So the 'outer appearance remains the same for all lanthanoids and as the inner orbitals do not influence the chemistry much, this explains the chemical resemblance of the REE. The physics indeed is not touched by this chemical fact so that the elements show different physical behavior. Characteristic for the lanthanoids is their common oxidation state of +3, whereas some REE show also other states (see Table 2.2). Preferred stable states are attained by empty, half or full occupied orbitals, i.e. La^{3+} (f^0), Gd^{3+} (f^7) and Lu^{3+} (f^{14}). Other stable configurations are Eu^{2+} (f^7) (which serves as a good reduction-agent), Yb^{2+} (f^{14}), Ce^{4+} (f^0) (as a good oxidation agent) and Tb^{4+} (f^7).

A specialty of the electron configuration is that with increasing atomic number the ionic radii get smaller; known as the lanthanide-contraction. This fact results in ionic radii of most trivalent REE similar to the radii of Ca^{2+} , Th^{4+} and U^{4+} . The slightly bigger Eu^{2+} has a similar radius to Sr^{2+} . This coincidence is important for the understanding of petrogenetic processes as most REE can and do replace elements with similar ionic radii. So REE can be found in rocks which contain Ca, Th, U and Sr.

For the physical characteristics, the REE show very diverse behaviors which make them especially useful for a wide range of applications. In magnetism some of the REE like Gd, Dy, Er but also Nd and Sm show complex potentials which can be and are used for magnets manufacturing [3, p. 394]. Some REEs provide sharply defined energy states which can be efficiently used in lighting and laser applications.

In summary there is a wide variety of similar and special characteristics inherent in the REEs. Especially the different atomic structures and states lead to some unique properties. Thus a complex and huge application field results from these properties which show similar but also completely different characteristics. This should give also an idea that REEs cannot be compared and dealt with as one single element.

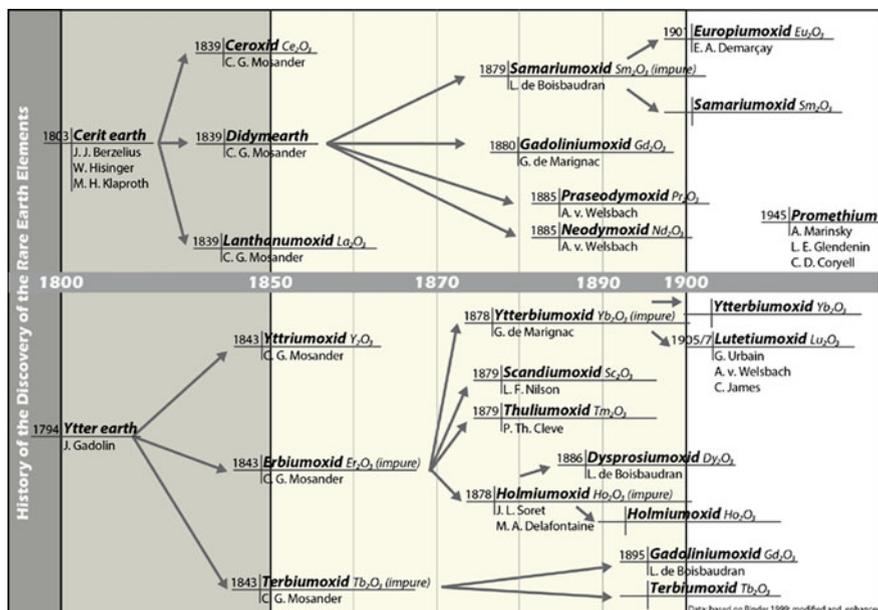


Fig. 2.1 History of the discovery of the REE

2.3 The Long History of the Discovery of the REE

The following story has been put together on basis of von Welsbach [24], Plohn [25], Greinacher [26], Trueb [27], Binder [10] and Brock [28]. They all give interesting insights in the long lasting discoveries of the rare earths (see Fig. 2.1). This is deemed interesting as it shows one of the basic problems: the separation of the individual REEs; which is still a decisive challenge today.

The fascinating story of the rare earths began around 1787 when the Swedish artillery officer Karl Axel Arrhenius, whose hobby was mineralogy, found a dark mineral in a feldspar pit near Ytterby, close to Stockholm. Greinacher [26] tells that the discovery leads back to a mine foreman who found a black mineral in 1788, which initially was called Ytterbite and later Gadolinite. The Finnish chemist Johannes Gadolin (1760–1852) studied this mineral and realized that this new material was of oxidic structure and called it ‘rare earth’. In 1794 finally, he discovered within that mineral a new element which was called ytterearth and later named Gadolinite. It turned out that in this mineral nine elements were hidden, but it took around 100 years to discover them all. Around 1803 the German pharmacist Martin Heinrich Klaproth (1743–1817) and the Swedish Jöns Jacob Berzelius (1779–1848) and Wilhelm Hisinger (1766–1852) discovered nearly at the same time but with independent effort another mineral in an abandoned pit near Bastnas, Sweden, which was later called bastnaesite. From that mineral they succeeded in the extraction of an element which upon heating showed a yellowish

material. They called it an ‘ochroite earth’ and later named it cerium, after the 1801 discovered small planet Ceres. Again this ceric earth contained its secrets nearly 100 years until the last ceric earth Europium was discovered [27]. Quite some time after Klaproth and Berzelius discovered the ceritic earth, it happened to the Swedish chemist Carl Gustav Mosander (1797–1858) in 1839, to separate the ceritic earth into the parts cerium (ceroxide), lanthanum (lanthanumoxide) and didym (didym-earth). Cerium often occurs in the so called Mischmetall to which it contributes about 50 %. The name lanthanum leads back to the Greek “lanthanein”, which means ‘being hidden’. The name didym originates on the Greek word ‘didymos’, i.e. twin, and was chosen due to the similarity of didym to lanthanum. It then took until 1879 when French Paul-Emile Lecoq de Boisbaudran (1838–1912) extracted samariumoxide from the didym-earth. Samarium was named after the Russian mining-clerk Samarsky, who also discovered the mineral samarskite. In this samarskite Boisbaudran demonstrated by spectroscopy the existence of samarium. In 1880 the chemist and professor Jean-Charles Gallissard de Marignac (1817–1894) from Geneva isolated another element out of the didym-earth, the gadolinium (oxide). The element was named after the chemist Gadolin. A further prominent scientist was the chemist Carl Auer von Welsbach (1858–1929) from Vienna. In 1885 he proved that didym-earth actually consisted of two elements: praseodymium and neodymium. The names were derived from the (Greek) attributes ‘praseios’ = leek-green (praseodymium—leek-green twin) respectively ‘neos’ = new (neodymium—new twin). Finally, in 1901 the French chemist Eugène Anatole Demarçay (1852–1903) succeeded in the discovery of the last ceritic earth, the europiumoxide. He extracted it out of the samariumoxide, which was thought to be chemically pure until that time. Named was europium after the continent Europe.

The ytter-earths as well can exhibit a similar history. After Gadolin presented the ytterearth in 1794, it took until 1842/1843 when Mosander extracted out of the ytterearth the ultimate yttrium, impure erbiumoxide and impure terbiumoxide. Mosander just shortly before discovered the cerium oxide and didym earth.

After another 30 years, in 1878, de Marignac could separate ytterbiumoxide out of that impure erbiumoxide. In 1879 further oxides could be extracted: scandiumoxide by the Swedish Lars Nilson (1840–1899), thuliumoxide by the Swedish Per Theodor Cleve (1840–1905) and (impure) holmiumoxide by the Geneva scientists Marc Delafontaine (1837–1911) and Jacques-Louis Soret (1827–1890). Scandium was named in honor of Scandinavia, thulium after the Nordic mythical island Thule and holmium after the Latin name of the Swedish capital Holmia. In the impure holmiumoxide de Boisbaudran found in 1886 the dysprosiumoxide. Its name was derived from the Greek word ‘dys’, which stands for ‘strenuous attainable’. The next to last discovery was in 1905 the separation of lutetiumoxide from the impure ytterbiumoxide which was demonstrated by three scientists independently from another: Auer von Welsbach, Georges Urbain and Charles James. The name goes back to the Latin name of the Paris, Lutetia. Finally, in 1945 in the USA, the radioactive element promethium was chemically isolated. This discovery was ascribed to both Jacob A. Marinsky, Lawrence E. Glendenin

und Charles D. Coryell. Named was promethium after the titan Prometheus out of the Greek mythology. He robbed the heavenly fire for the humans. Other scientists were not as successful as the ones described. One of the *unlucky* scientists was William Crookes who tried to identify the individual REE by means of the—at that time new—radiant spectroscopy. It turned out however, that impurities in the mineral prevented him in participating in the discovery of the REE during the Rare Earths Crusade [28].

Eventually it took more than 150 years to identify and discover all 17 rare earth elements. The first important use and economic application goes back to Auer von Welsbach. He was, next to being a brilliant scientist, also interested in the commercial use of his findings. First von Welsbach soaked woolen threads with salts of the rare earths and put the threads to the flame of the Bunsen burner and realized that this was the first real light source, as until that time light was more a byproduct of heating. Such the Auerlight was invented. Von Welsbach managed, by use of fractionized crystallization, to separate the individual rare earths. Initially he used lanthanum, later primarily thorium oxide and about 1 % cerium for the lamps. The main raw material was ballast, monazite sand, of Brazilian ships which was abundantly available so that cerium was there in excess. Then von Welsbach melted cerium with iron and thus discovered the Auermetal, a prerequisite for lighter flints, which are still used today. At that time also the functional use of Ce for glass production and UV protection was discovered [25]. So the first commercial applications for REE were the Auerlight, flintstones and the use of RE fluoride as wicks in arc light carbons [26].

2.4 Geology and Geochemistry of the REE

At first a short explanation of geological and mineralogical terms seems appropriate, as these definitions are usually unfamiliar to non-mineralogists and non-geologists. Knowing these backgrounds can contribute to minimize the inaccuracies around the availability of the REE.

A mineral is a chemically homogenous, naturally formed part of the earth. With a few exceptions minerals are inorganic, solid and crystalline. A crystal is a solid, homogenous and anisotropic body with a three-dimensional periodic array of the components, i.e. atoms, ions or molecules. Here the elements are addressed. Rocks are comprised out of mineral aggregates and form vast geological bodies. Ores are rocks or mineral aggregates which contain metals or metallic compounds. A spatially confined area of concentrated minerals is called occurrence and if it is exploitable the words *deposit*, *ore deposit* or *mineral deposit* are used. Specific details are given in mineralogical literature (e.g. [12, 14, 19, 29, 30]).

The basic principles of petrogenesis are known to a certain degree today so that potential REE aggregations, occurrences and deposits can be judged reasonably well. The geochemical behavior of the REE and above all the ionic radii are responsible for the enrichment of REEs. The ionic radii of common rock forming

elements like aluminum, chromium, iron or sulfur are smaller than the ones of the REE, so that the REE cannot be built into the crystal structure of general rocks. So they are no major rock forming elements, instead they aggregate in residual fluids and enrich there as accessories [29, 31].

All REE are lithophile elements, i.e. they occur together with oxygen usually in oxide, silicate or phosphate combinations. As well, REE never occur in pure, i.e. native form but always together with other REE as accessories in minerals. There is mainly an aggregation as LREE or HREE and some complex mineral ores [23]. Typical REE minerals are monazite and bastnaesite with high grades of LREE or ceritic earths and xenotime which contains higher grades of HREE or ytter earths. Further REE containing materials are the ion-adsorbing clays, which are residues from alteration. Today several hundred REE containing minerals are known, however only very few have been identified to be of economic importance.

In general rare elements can enrich under magmatic processes. Often the REE enrichment is tied to partial anatexis (melting of parts of the earths' crust) and the subsequent magmatic differentiation, i.e. fractionized crystallization. The elements aggregate during several steps in fractions of similar or compatible shape. The complex processes shall not be explained here as they are well explained in respective mineralogical and geochemical literature as stated above.

Typical occurrences of REE are in granites, pegmatites, carbonatites and perovskites [12]. Granites together with other rocks represent the most important group of plutons (magmatic rocks which crystallized below the surface). Pegmatites are coarse to huge grained magmatic rocks which can contain single crystals with sizes of several meters. In principle plutons can be shaped as pegmatites. Carbonatites are of intrusive character and thus connected to volcanic active intracontinental rift-zones but also hot-spot-areas. They are usually enriched with phosphate-minerals like apatite and monazite, but also bastnaesite and others. Perovskites are oxidic combinations of a metal and oxygen, in this case CaTiO_3 , whereas Ca can be replaced by REE. Perovskites occur as accessories in Carbonatites and some other magmatic formations [12]. A look at the present REE deposits reveals the just mentioned geological formations. Consequently, potential future mines are found in similar rock formations. Further details are given by Okrusch and Matthes [12], Stosch [19] or Mason et al. [14]. Several authors provide lists with REE containing minerals and deposits, e.g. Kanazawa and Kamitani [32]; Jones et al. [33] and Orris and Grauch [34]. Especially Jones et al. [33] give a vast list of about 200 known REE containing minerals. Elsner [35] states, that monazite and bastnaesite are the major minerals worth mining. Both are containing mainly LREE. Another relatively abundant mineral is xenotime which contains HREE, specifically yttrium, but also dysprosium, holmium, erbium, thulium, ytterbium and lutetium [35, p. 92f]. Furthermore the RE containing clays or ion-adsorbing clays, which occur mainly in southeast China, shall not be forgotten as they provide the majority of HREE nowadays.

Monazite, usually shown as $[(\text{Ce}, \text{La}, \text{Y}, \text{Th}) \text{PO}_4]$ [29], sometimes a bit simpler as $[\text{Ce}(\text{PO}_4)]$, can also incorporate Nd and Th as these can substitute Ce within the monazite [12, p. 116]. So either way the possible accessory element Th represents

the *problem* as Th is radioactive and requires special handling. During mining and processing the material has to be handled according to specific laws and regulations. And not to forget, the tailings have to be treated in accordance to the regulations as well, what poses a big challenge. This does not mean that monazite cannot be mined, but the handling associated with radioactive materials handling is intensive both in time and cost. At the beginning of the 20th century REE mining was predominantly from monazite so that the first era of REE mining is called the *monazite-era* [36]. Monazite is primarily found in granites, pegmatites and carbonatites. Monazites secondary occurrence is as placer deposits, marine and beach sands. Together with rutile, ilmenite and zirconium, monazite occurs as heavy sand deposits and was mined around the 1950s in several countries, e.g. as beach sands in Florida, USA or placer alluviums in Idaho, USA (Bureau of Mines, [37], p. 1178), in Australia, India or Brazil. The heavy sands mining activities have been reduced, mainly due to the radioactive materials handling challenge.

Bastnaesite, a fluorocarbonate mineral, is the other important mineral in REE mining. The basic chemical formula shows [(Ce, La) (CO₃) F] whereas varieties exist with different balances of La and Ce. Next to the given formula also other LREE can be contained like Pr, La but also Y (e.g. [31, 33]). Bastnaesite is the main mineral that was exploited in the Mountain Pass Mine, California, USA. This mine gave name to the era following the monazite-era: the *Mountain Pass Era*.

Xenotime, [(Y, Yb) (PO₄)], another phosphate contains higher grades of HREE, especially Roskill [17] states that the four mentioned minerals, monazite, bastnaesite, xenotime and the lateritic clays account for about 90 % of the economic production. Table 2.3 details in more depth the typical elemental contents of the minerals mined at present, respectively in near future (the Mt. Weld churchite).

Table 2.3 shows various deposits and their typical RE contents. It can be seen, that monazite and bastnaesite provide high percentages of the LREE whereas the HREE only occur in very small percentages, sometimes only in traces. The xenotimes and lateritic ion adsorption clays show a relative diverse spectrum with a clear emphasis on HREE. Roskill [17] provides slightly different data, which they extracted from NDRC, metal-pages and direct contacts with RE processors. It has to be noted eventually that these contents data represent average values. The mineral compositions may and obviously do differ from ore body to ore body and sometimes even within one ore body; variations and changes are common.

In 2011 a team of Japanese scientists discovered a new geological setting as a new potential resource for REE in the Pacific Ocean. They measured more than 2,000 seafloor samples and found high concentrations of REE and Yttrium within some of the samples. From these samples estimates were derived which show huge REE quantities available. The concentrations and mineral compositions show promising structures which would allow relatively easy refining. However, the team clearly stated that the samples were taken from depths mostly between 4,000 and 5,000 m, and they as well estimate that an extraction *today* is not possible. Eventually the discovery then shows a potential for mid to far term future extraction [38]. Indeed the occurrence of REE in deep-water polymetallic nodules is known long since and is investigated in several projects in these days (e.g. ISA,

Table 2.3 Elemental composition of selected REE minerals

Deposit	Mt Weld CLD	Mt Weld Duncan	Mountain pass, CA	Bayan Öbo, Inner Mongolia	Guangdong	Xunwu, Jiangxi	Longnan, Jiangxi
Country	Australia	Australia	USA	China	China	China	China
RE mineral	Secondary monazite	Churchite	Bastnaesite	Bastnaesite	Xenotime	Laterite	Laterite
Lanthanum	25.57	23.93	33.2	23	1.2	43.4	1.82
Cerium	46.9	39.42	49.1	50	3	2.4	0.4
Praseodymium	4.92	4.85	4.34	6.2	0.6	9	0.7
Neodymium	16.87	18.08	12	18.5	3.5	31.7	3
Samarium	2.29	2.87	0.8	0.8	2.2	3.9	2.8
Europium	0.49	0.77	0.1	0.2	0.2	0.5	0.1
Gadolinium	1.33	2.15	0.2	0.7	5	3	6.9
Terbium	0.13	0.29	Trace	0.1	1.2	Trace	1.3
Dysprosium	0.31	1.36	Trace	0.1	9.1	Trace	6.7
Holmium	0.04	0.21	Trace	Trace	2.6	Trace	1.6
Erbium	0.113	0.46	Trace	Trace	5.6	Trace	4.9
Thulium	0.01	0.04	Trace	Trace	1.3	Trace	0.7
Ytterbium	0.05	0.2	Trace	Trace	6	0.3	2.5
Lutetium	0.02	0.03	Trace	Trace	1.8	0.1	0.4
Yttrium	0.95	5.36	0.1	Trace	59.3	8	65
Checksum	99.993	100.02	99.84	99.6	102.6	102.3	98.82

Notes and sources

Lynas [87] Roskill international Rare Earths conference presentation. 16. Nov. 2011

USGS and Hedrick [88] Minerals yearbook 2000. Rare Earths. Hedrick assembled a comprehensive list of deposits and their RE contents. For each deposit further data sources are given

Data given in (% REO)

w.y.) Here the already known static range of 850 years (on land) has to be set as a contrast. There is no physical or mineral shortage, but rather a technological and probably economical issue to be solved. So the usefulness of deep-water mining has definitely to be seen in this context.

2.5 Deposits, Current and Potential Future Mining

In summary of the chemistry and geology of the REE it can be said that the petrogenesis of the REE is reasonably well known. In turn potential and possible occurrences can be derived and are more or less well known since a while already. There is also evidence of deposits in several places of the earth. Gupta and Krishnamurthy [39], Orris and Grauch [34], Jackson and Christiansen [40] or Berger et al. [41] give comprehensive information and lists of known mines, deposits and occurrences. So even before the increase of interest in REE since about 2008, it was known that from a geological point of view there is no physical shortage of REE. The USGS in 2011 announced the REE reserves with 110 Mio t which equates to a static range of approximately 850 years [42]. Still, that value seems to be too low as today around 180 companies work on about 270 projects around REE prospection, exploration and mining [43]. Not all of these new prospection and exploration data are incorporated yet in the data given by the USGS. Looking at these facts, a strange contradiction becomes apparent. In principle there should not be a shortage situation. But it does actually exist! At least that is, what the media tell us. So the question again is how and why this can be or asked the other way around, what is actually the case? Is there a real shortage or is it only an anticipated shortage? And if a real shortage situation should exist and there is a range of 850 years, what good for is the information of 850 years of range? If nothing happens, this static range is of no practical use at all. Usually the monopolistic position of China is put into the field, which could or would prohibit new mining ventures. Of course this scenario is possible, but the question remains whether that is a reasonable argument for not pursuing any steps but pointing fingers at China instead? These questions should raise the awareness, that there is more than just one problem involved. Nevertheless the facts contain potential solutions. Having this in mind the status quo of REE mining and deposits will be illustrated briefly together with the description of some projects which are said to start production within the next one to three years. The ordering has been done by country and alphabetically.

2.5.1 China

The three major mining areas in China are in Baotou, Sichuan and Jiangxi which together host 88 % of the Chinese deposits. Affiliated to Baotou is the Bayan Obo mine in Inner Mongolia where 83 % of the Chinese deposits are concentrated. In

Sichuan province as well as in the southern deposits 3 % each are located. The remaining 11 % are dispersed throughout China [44]. The largest mining site is situated in Bayan Obo, Inner Mongolia, which belongs to the Baotou Iron and Steel Corporation. The huge polymetallic REE-Fe-Nb deposit is exploited with iron being the primary product and REE and Nb being secondary or by-products. The principal REE minerals in Bayan Obo are bastnaesite and monazite with major Ce, La and Nd contents [45].

In Bayan Obo REE mining began in the late 1950s, even though the deposit was discovered already in the late 1920s. Today the REE are mined as a by-product of iron ore mining. More detailed information is provided by Hurst [1] and the archives of the Bureau of Mines (today: USGS), 'Minerals yearbook metals and minerals (except fuels)' in the chapters 'Minor metals' and later in own chapters about 'Rare earths'.

Wu et al. [46] show that the elemental distribution of the Bayan Obo bastnaesite and monazite are very similar and comprise about 26 % La_2O_3 , 50 % Ce_2O_3 , 5 % Pr_2O_3 , 16 % Nd_2O_3 , 1 % Sm_2O_3 and the remaining REE less than 1 % each.

A further important formation is situated in Mianning, Sichuan, called the *Mianning-Dechang Himalayan REE Metallogenic Belt* along the Yangtze Craton. Scientists discovered five potential REE deposits in the carbonatite [47, 48]. The Sichuan mines exploit bastnaesite with about 37 % La_2O_3 , 47 % Ce_2O_3 , 4 % Pr_2O_3 , 10 % Nd_2O_3 and all others below 1 %. An interesting side note is that Sichuan lies in a potential earthquake zone. The strong 2008 Sichuan earthquake occurred along the Longmen Shan fault which is close to the mineral belt. Mining projects thus have to keep in mind potential additional dangers from tectonics.

In southeastern China REE containing lateritic clays are known. In several provinces around Jiangxi these ion-adsorbing clays are exploited which show very diverse distributions ranging from 2 to 30 % of La_2O_3 , 1–7 % Ce_2O_3 and Pr_2O_3 , 3–30 % Nd_2O_3 and 2–7 % Dy_2O_3 [46, table p. 291]. These southern provinces are featured as middle to heavy REE deposits where mainly Gd to Lu, Sc and Y are mined [44]. As especially Dy is required for improving the temperature stability of NdFeB magnets, these deposits are of great importance. However, there are concerns about these deposits as "...their ion absorption [sic!] (laterite) clay deposits are expected to be depleted by 2025 or earlier. This leaves them [China] with only one known xenotime deposit in Guangdong as their primary source of heavy rare earths". [49, p. 6].

Further occurrences of REE have been discovered in weathering crusts of basalt in Yunnan, Guizhou and Sichuan provinces which are subject of further research for potential new deposits (Yang et al. [50]). Occurrences and deposits are also probable in the Tsagaan region in Mongolia and China [51]. More research information is given e.g. in the Journal of Rare Earths.

2.5.2 India

In India the production of REE products is under the control of the Indian Rare Earths Limited (IREL), a governmental undertaking under the administrative control of the department of Atomic Energy. It was founded in 1950 with the primary intent to produce monazite in a commercial scale for the recovery of thorium. Today IREL operates four units, the Orissa Sand complex (OSCOM), the Chavara Mineral Division, the Manavalakurichi (MK) Mineral Division—all exploiting mineral sand deposits, and the Rare Earths Division (RED) in Aluva where a chemical plant processes monazite produced by MK. It is stated, that only MK produces 3,000 t of monazite per year and that RED has a production capacity of 3,600 t of monazite. REE products, Ce, Nd, Pr and Sm are offered in different grades and states. The major product however does not seem to be REE, instead the emphasis is on thorium and uranium in mantle grade quality and the export of titanium oxide as pigment [52]. The USGS usually lists India as a producer of REE with an annual production of 2,700 t [42]. This value hasn't change since years. Both data sets, the ones from IREL and USGS, cannot be proofed for reliability and validity.

2.5.3 Brazil

In Brazil heavy sands mining is known since the turn of the 20th century. Several mining areas which exploit heavy and monazite sands are dispersed throughout Brazil with five areas encompassing REE rich sands, including also thorium and uranium: Buena, Cumuruxatiba, Guarapari, Mato Preto and Sapucaí all located in the southern and southeast regions. The beginning of the monazite mining can be traced back to the invention of the Auer-Light which required cerium and thorium for production. As well thorium was used in therapeutic applications so that the thorium refining industry experienced a boom during the first decades of the twentieth century [53, p. 190f, 54]. Today there is a problematic legacy associated with the mining of monazite and the naturally occurring radioactive materials (NORM). As the tailings have not been treated cautiously enough, there are several contaminated areas which require repeated site remediation, as previous works have not been accomplished accordingly. Today Brazil tries to improve future actions and NORM handling based on the lessons learned from previous monazite processing [55]. The present monazite mining and processing is under the head of the national atomic agency, the *Indústrias Nucleares do Brasil* (INB) [56]. In 2005 and 2006 the INB produced 958 t of REE out of monazite heavy sands, without further detailing the elemental share [57]. The USGS gives no production data for Brazil in 2005 and 2006 so that even when taking into account that the USGS states 400 t for 'Other countries' in 2006 [58] that does not match and cannot reflect the data given by Rezende [57]. This inconsistency in data again shows the persisting informational dilemma.

2.5.4 Russia, Commonwealth of Independent States and Kazakhstan

Reliable data about Russian production could not be derived. Several sources as mentioned at the beginning of this paragraph state present production or at least potential deposits in Russia and the CIS. The most promising being the Afrikanda complex, Kola peninsula [59], the Khibina and Lovozero alkaline massifs on the Kola peninsula [60] and the huge Tomtor massif in eastern Siberia [41, 61]. For this Tomtor deposit an exact and reliable geographical position could not be determined, rather three possible locations are likely, one being near the city of Yakutsk, the next near the city of Oymyakon, attributed the coldest city of the world, and Berger et al. [41] suggest a position about 1,100 km northwest of Yakutsk. Nevertheless all of the three positions have in common that they are on permafrost soil and they all lack transportation and energetic infrastructure. If this deposit would be exploited the climate, energetics and logistics would pose a big challenge.

Further deposits are supposed to be in Kutessay, Kyrgystan, however no reliable data are available [21].

2.5.5 Australia

In Australia several deposits are known. Initially REE were extracted from beach or heavy sands as a byproduct of titanium mining. The most promising deposit today however is the Mt. Weld mine in Western Australia owned by Lynas Corp. Ltd. Extraction is supposed to start as soon as the Lynas Advanced Materials Plant (LAMP), situated in Malaysia, gets into full commission. This processing facility was the bone of contention as the population raised concerns about the radioactive materials (i.e. thorium) handling associated with the plant. Finally the International Atomic Energy Agency (IAEA) issued a file and reported that they had not found any non-compliance to any IAEA safety standards, however 11 recommendations were issued [62]. The Malaysian government followed these recommendations (Malaysia MTI [63]) which were fulfilled so that the Board announced its approval for a temporary operating license on Feb 2, 2012 [62]. The plan is to ramp up production to 22,000 t REO annually in two steps.

Further projects are the Dubbo Zirconia project by Alkane Resources Ltd., the Nolans project by Arafura Resources Ltd. next to some smaller other ones.

2.5.6 USA

The REE mining in the US began as monazite or heavy sands mining when REE mining was more or less a byproduct of thorium and uranium mining [64]. Major

mining activities were in Florida and Idaho where beach sands and placer alluviums respectively were mined. Furthermore monazite sands were known in South and North Carolina, in Lemhi County, Idaho; Wyoming, Alaska and Montana [37, 65]. Exact production data were usually kept secret as the material was needed for the atomic and nuclear energy industries. The radioactive material handling accounted for much of the production price of the raw materials [64, p. 1387]. This additional effort and cost was the main reason for the eventual abandoning of most of the former heavy sands mining activities. It is interesting to note that the names of these old acquaintances appear again nowadays as promising potential new deposits: Lemhi Pass, Idaho and Montana; Diamond Creek, Idaho; Bear Lodge, Wyoming, and Bokan Mountain, Alaska [66, 67].

In early 1949 bastnaesite was found in the Mountain Pass district [68] when subsequent geological mapping showed mineable deposits within the Sulphide Queen Carbonate body which proved as the worlds' greatest concentration of REE known at that time [69]. In 1952 the rare earth open pit mining began under the head of the Molybdenum Corporation of America which was later renamed into Molycorp. The facility also did the beneficiation and processing to provide several REE products. The invention of the color TV in the mid-1960s required considerable amounts of Eu which pushed production [70] and Mountain Pass became the primary REE production facility in the world while the importance of monazite mining diminished. In 1985 ground water samples brought evidence of leaking evaporation ponds due to mechanical failures. Despite remediation activities further contaminations have been identified which contributed arguments to the shutdown of the mining and production facility on Mountain Pass eventually in 1998/2002 [70, 71]. The other argument for the closure at that time was the strong position of Chinese mining projects, which offered REE products cheaper than the U.S. did. In the course of the action of increased focus and demand for REE in 2004 Molycorp finally attained a new 30 year mine plan permit. In 2007 the extraction from tailings was restarted. According to the company's homepage, a full up operation is planned to effectively start in late 2012 with a scheduled production capacity of 40,000 t of REO annually. The idea incorporates the Phoenix Project which is to modernize the installations, and basically to offer an efficient "mine-to-magnet" supply chain. For this, the company attained shares in several downstream businesses like production facilities, magnet producers, wind energy and recycling of REE.

2.5.7 South Africa/Canada

In South Africa the former producing Steenkampskraal mine is planned to reopen production in 2013, according to Great Western Minerals Group [72]. The mine was in operation from 1952 until 1963 when monazite was extracted from underground mining with a subsequent processing in the United States. GWMG, the owner of the mine today, states the aim to become a fully integrated rare earth

producer. The company therefore invested in a chain of downstream businesses like exploration projects in Canada, an rare earth alloy processing facility in the UK, and a joint venture with a Chinese company to install a separation facility near the mine at Steenkampskraal [73]. A further South African project is the Zandkopsdrift site [74].

2.5.8 Others

Hatch [75] assembles and updates an ‘Advanced Rare-Earth Projects Index’ where he lists these projects which fulfill certain criteria concerning resource and reserve numbers and basically the knowledge and capability to actually start a mining project. Out of nearly 400 projects known in mid-2011, twenty projects fulfill these criteria. Next to the projects mentioned above, there are the following enterprises included: Eco Ridge, Eldor, Hoidas Lake, Nechalacho (Thor Lake), Strange Lake and Zeus (Kipawa), Canada; Kangankunde, Malawi; Kvanefjeld and Sarfatoq, Greenland and Nora Karr, Sweden. The German BGR lists several further projects foreseen as exploitable deposits located in southern Africa, Canada, the US, Argentina, Madagascar, Vietnam and Indonesia. Occurrences are even more widespread and including areas in Brazil, Saudi Arabia, Europe and Mongolia (Steinbach et al. [43]).

In summary there are several promising projects in quite advanced stages of development. In how far these projects actually will be realized is not known and will not be commented. Next to the already mentioned projects many others are pursued, but it cannot be verified, how far these projects actually have developed. Several reports are provided by financial analysts and consultants who try to suggest successful investments. This intent often lacks scientific clarity and reliability so that they are not evaluated in this work. As for Hatch [75] and the BGR it can be assumed, that they consider projects which fulfill commonly accepted and expected standards. These are primarily the JORC, the Australasian Code for Reporting of exploration results, Mineral Resources and Ore Reserves. “The JORC Code provides minimum standards for public reporting to ensure that investors and their advisers have all the information they would reasonably require for forming a reliable opinion on the results and estimates being reported” [76].

One more important argument when talking about new mining projects is the required timeframe for opening up a new mine. The development of a mineral exploitation is roughly divided in five to six phases. Starting with the *Mineral Resource Assessment* there follow the *Mineral Exploration Phase*, the *Mineral Deposit Appraisal* and the *Mine Complex Development*. Until this phase about 5–10 years’ time are usually necessary. The required timeframe depends, next to the geological-mineralogical issue, on the jurisdictional facets like ownerships and licensing. Then the *Mine Production* as such exploits the raw material and finally the last phase of *Reclamation and Environmental Restoration* ends the process. Details are well explained in USGS [77], NRCAN [78] and NRCAN [79].

To conclude this chapter it should have become clear, that there indeed are several deposits which could and will be exploited; nearly all of them are outside of China. These could provide enough raw materials to satisfy demand. So it is not a physical scarcity problem, but more a lack of intent, will and probably funding to start new projects. Maybe also the HREE deposits are still not very promising. Details about estimated and projected quantities are described e.g. by Liedtke and Elsner [80] or Hatch [74]. But even when a new project starts, that does not yet mean, that all problems are solved and production does flow; as the example of Lynas and their separation facility shows. Especially the processing and separation of the REE is the real challenge and the environmentally relevant problem; not the mining activity itself. Finally, one fear or possibility remains, that China could change prices of REE on purpose so that potential new mining ventures would become non-profitable from the very beginning onwards. Here however, China issued that it is not the intent to misuse its monopolistic situation as China expects a growing domestic demand so that they are dependent on imports of REE in a midterm timeframe [44].

2.6 Rare Earth Processing

The RE processing is a very important but also complex issue and not very often described in reports. The importance is as such, as for the separation into the individual REE intensive operations are required both as physical and chemical treatment to get the REE. The used chemicals as well as the tailings bear potential hazards to the environment. The processes will only briefly described as e.g. Gupta and Krishnamurthy [39] give some very in depth insights into the various common processes. As well some historical insight is given into the Chinese hydrometallurgy technology in the Journal of Rare Earths [81].

In principle the steps for REE production can be divided in four phases: first there is the mining process as such where REE containing ores are usually mined from open pit projects. Second is the physical beneficiation during which REE concentrates are gained. Then the chemical treatment extracts oxide products which are subsequently separated using extractive metallurgy to get the individual REE.

After the ores are broken or the heavy sands are mined, the raw materials are treated to gain concentrates. These then are chemically treated using acid and alkali solutions. After this initial chemical treatment, the separation is initiated by a variety of processes:

The various processes for separating individual rare earths from naturally occurring rare earth mixtures essentially utilize the small differences in basicity resulting from decrease in ionic radius from lanthanum to lutetium. The basicity differences influence the solubility of salts, the hydrolysis of ions, and the formation of complex species, and these properties from the basis of separation procedures by fractional crystallization, fractional precipitation, ion exchange, and solvent extraction [39, p. 158].

As some REE appear, next to their trivalent state, also in further states this feature can be used to extract the REE by successive selective oxidation and reduction processes.

The *fractionized crystallization* process is suited for the ‘lanthanum end’ where the ionic radii differences are the biggest. For Tm and Ho however the process is extremely intense and time consuming. According to Gupta and Krishnamurthy [39], it takes about 15,000 recrystallization processes to obtain close to pure Tm and about 4 years of repeated crystallization processes to extract Ho from rare earth bromate. For this process several salts and double salts are required. The *Ion Exchange* method is a commercially used method.

The fact that it is feasible to separate a mixture of 15 rare earths into components exceeding 99.99 % purity in one pass through the system and that the process can be scaled up to multi-tonne quantities, with possibilities of recovering and recycling water, and retaining ion and complexant, has led to the continued commercial use of ion exchange even after the entry of solvent extraction in the field. A major limitation... is that the technique is inherently a batch process [39, p. 168].

Hence the Solvent Extraction is a favorable method with the advantage of compact equipment. The process itself is relatively fast, continuous and is suitable for handling of large quantities. The Ion Exchange method is still considered superior in the production of extremely pure materials [39, p. 193].

So in general there are methods known on how to separate the REE. Yet there remains the problem of environmental damage by processing REE, i.e. the handling of chemicals before, during and mainly after the processing. This poses the real threat to the environment next to the radioactive materials storage of some tailings. Basically all known mishaps in the REE mining and processing were due to the toxication of the environment due to spilled chemicals.

2.7 Applications for REE

The applications for the REE cover a huge field as all 17 elements have to be considered. Despite their chemical similar characteristics they have diverging applications. First a list of the major REE uses and applications is given.

2.7.1 Applications of the Individual REE

A list of applications attributed to the individual REE is attached in Annex D. The range of applications within one element changed over time and got more diverse as innovation leapt forward. In the case of neodymium for example the element initially was used for coloring glass whereas today the major use is for the

manufacturing of permanent magnets. So around the beginning of the 20th century all neodymium was used for and within the glass industry; today that share became modest and the major share is for magnets production. As this principle is applicable to all individual REE, the list is long and it should become apparent again that a simple grouping of all REE together does not address the diversity of the 17 elements adequately. Either the single REE should be considered individually or at least as part of an application field like the (permanent) magnet production or the glass industry. But this renders a qualitative and quantitative determination difficult as obviously one element can be part of several application fields. Scientific literature gives some extremely detailed insight into various research and scientific fields, especially the book series ‘Handbook on the physics and chemistry of rare earths’ edited from the beginning in 1978–2010 by Gschneidner and others, since 2011 edited by Bünzli and Pecharsky (Gschneidner and Eyring [82, 83]). With less detail but with more emphasis on the whole life cycle of rare earths, e.g. Gupta and Krishnamurthy [39] and Delfrey [84] cover some REE in quite good detail.

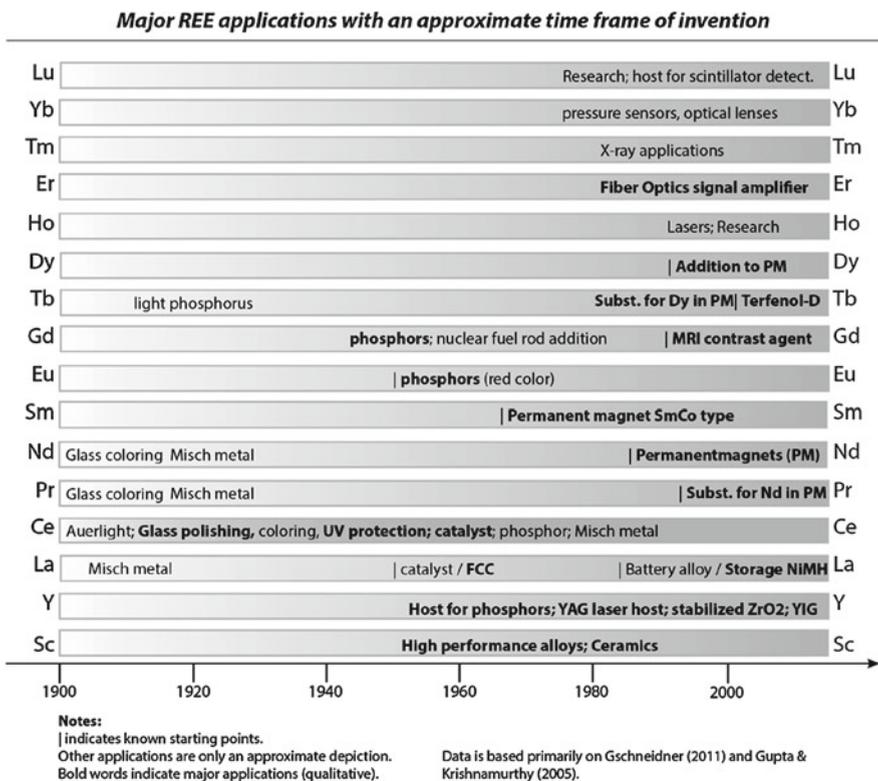


Fig. 2.2 Major REE applications in a historical context

2.7.2 Major REE Applications in a Historical Context

Figure 2.2 shows the major REE applications by element together with a rough depiction on the year of invention for commercial use.

The application—time depictions in Fig. 2.2 do not represent hard dates but rather give a general idea of the beginning of specific uses in about 5–10 year frames. For an overview this depiction is deemed accurate enough; which does not preclude further in depth analysis of selected single cases of invention.

2.7.3 Applications of REE According Functional Uses

Another listing or grouping of REE along application fields or functional use is regularly seen at Chegwiddden and Kingsnorth [85] and Lynas [86]. They use the following fields: *magnets, metallurgy, battery alloys* (sometimes included in metallurgy), *ceramics, polishing, glass, phosphors, catalyst* and *others*. A brief arrangement of these applications and the REE used therein is given in Fig. 2.3.

This graph gives an overview of the REE needed in respective functional areas. It would be important to state as well the relative share of the REE to the functional fields. This data set is so far not available and is also subject for further research. This would give a better idea of the real critical areas and potential competitive applications so that appropriate actions could be initiated.

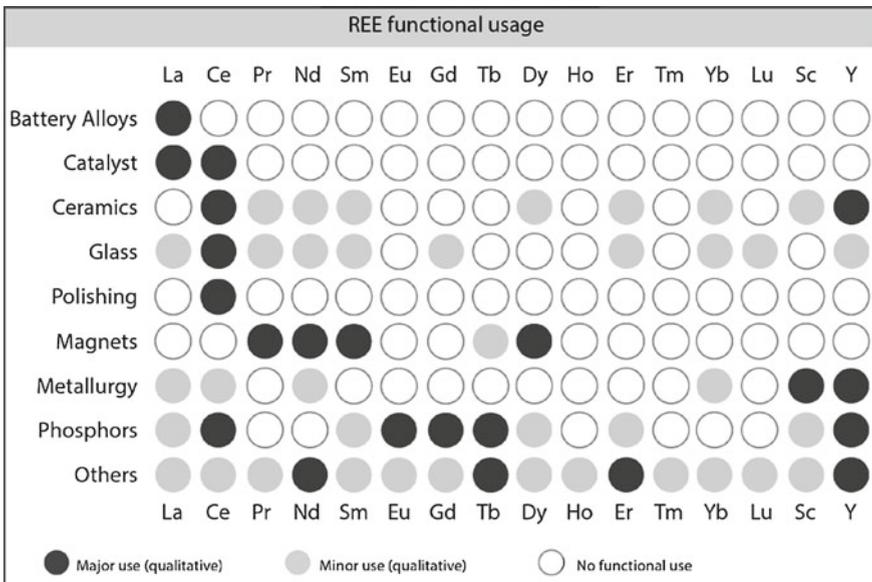


Fig. 2.3 REE and their respective functional use

Applications containing REEs

Area	(Energy) Efficiency	Environmental Protection	Digital Technology	Medical Applications	Military Applications	Others
Objective	reduced consumption	reduced emissions	lifestyle & communication	improved therapy	mobility & reduced weight	better life
Product examples	<ul style="list-style-type: none"> Lighting, LED FCC Permanent magnets - smaller size products e-mobility - electro motor Alloys - reduced car weight Glass - color & UV protection 	<ul style="list-style-type: none"> Wind Turbines (Direct Drive REE magnet based) Car catalytic converters Diesel fuel additives 	<ul style="list-style-type: none"> Flat Panel Displays (FPD) - glass, LED Hard Disk Drives (HDD) Mobile communication systems Fiber optics, signal amplifier 	<ul style="list-style-type: none"> Magnetic Resonance Imaging (MRI) X-ray systems Medical additives and contrast agents Lasers 	<ul style="list-style-type: none"> electro motors for propellant systems, sensors, guidance systems special materials (Terfenol-D) Energy storage (Batteries) Electro-Motors 	<ul style="list-style-type: none"> Y x G - Lasers (super)alloys Superconductors Neutronabsorbers Algae control Water treatment Magnetic refrigeration

Fig. 2.4 Applications containing REEs

2.7.4 Applications of REE According Present Discussions About Climate Relevant Uses

A last arrangement is getting more common and was used by Lynas [86] and amended by the author as shown in Fig. 2.4. Here the emphasis is along the present focus on climate relevant issues and uses.

The sorting in Fig. 2.4 is as follows: **energy efficiency** incorporates systems that use less energy like modern energy saving lamps, LEDs but also hybrid cars with e-Motors that reduce gasoline use. Special alloys allow a reduced vehicle weight and thus contribute to less fuel consumption. Finally glass with respective UV protection can help to reduce energy use in buildings. The **environmental protection** block strives for reduced consumption but in a more direct way, i.e. to reduce emissions. WTG reduce the need for carbon based power plants, and catalysts help to clean exhaust emission. The **digital technology** definitely is not in direct ties to climate issues but a contribution to lifestyle and communications. One could argue that this technology allows doing video conferencing and thus saving some travels; if that really is the case is another issue. Nevertheless do some REE allow the manufacturing of modern gadgets which are deemed indispensable for today’s life. **Medical applications** are primarily seen as MRI systems, X-ray supporting materials, contrast agents, medical and surgical lasers. **Military applications** have a very strong focus in the US but can mainly be reduced to the applications used in the civil world. I.e. the military requires electro motors using permanent magnets both for weapon systems and expendables like bombs, rockets, etc. They also need computers, communication gadgets, special lightweight steels, glass for several applications or storage systems. There are some materials like Terfenol-D which are predominately useful for military applications. Finally a

block **recent and developing** is kind of a bin for the most recent developments like lasers, signal amplifiers, super conductors, water treatment or magnetic refrigeration. Of course this arrangement is of discursive character.

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