

Rare Earth Elements (REE)

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The rare earth elements (REE) comprise a group of 16 chemically very similar elements that occur widespread in rocks, soils, and water bodies, share similar ionic radii to the essential element Ca^{2+} , and consequently also occur in biota. Given that REE form mainly trivalent cations, they also share similarities to Al^{3+} . Compared to their chemical cognate Ca, they have a higher reactivity. Thus, their accumulation in soils may constitute a severe environmental threat. Over the last decades, the increasing use of REE in modern technology and fertilizers raised concerns about the pollution of soils and water bodies, which led to a rapidly increasing number of publications dealing with REE toxicity to plants, animals and humans, the fate of REE in soil–plant systems, REE cycling in ecosystems and impacts of REE pollution on food security.

Keywords: biosphere ; hydrosphere ; lithosphere ; pedosphere ; availability ; soil fractions ; complexation ; rhizosphere ; toxicity

1. Introduction

The initial technical application of rare earths took place at Althofen in Carinthia, Austria. Today's Treibacher Industrie AG was originally founded in 1898 at the site of a former Fe-smelter by Carl Auer von Welsbach. Auer von Welsbach discovered the rare earth elements Pr, Nd, Yb, and Lu, and had produced REE-based “flints” as essential parts of lighters, which are still produced today, beneath other Zr, V, and Mo-based products and compounds ^[1]. In recent years, due to the intense mining and processing of rare earths, much has been published about environmental contaminations and interactions with biota, and the environmental effects of REE have become of increasing concern.

The rare earth elements (REE) comprise 16 chemically very similar elements from the group IIIB of the periodic table, including 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 (Tm), ytterbium (Yb) and lutetium (Lu), yttrium (Y), and there are similarities to scandium (Sc) ^[2]. Despite their name, REE are, in fact, not rare but occur widely in minerals, rocks, soils, and biota at concentrations comparable to essential micronutrients. Specifically, in the Earth's crust, the average concentrations of REE vary from 66 mg/kg (Ce) to 0.3 mg/kg (Lu). The sum concentrations of all REE together (150 mg/kg) and even the concentrations of individual elements from this group, such as Ce, are higher than the more studied essential trace metals Ni (75 mg/kg), Cu (55 mg/kg), and Zn (70 mg/kg) ^{[3][4]}. Irrespective of their absolute concentration level in different environmental compartments, which vary considerably, the concentrations typically decrease with increasing atomic number. Moreover, REE with even atomic numbers are more frequent than their neighbors with odd atomic numbers according to the Oddo–Harkins rule. Compared to other elements from the periodic system, no other group with a uniform oxidation state displays such a remarkable similarity as REE ^[5]. As a unique feature in this group, all 16 REE exhibit ionic radii similar to Ca^{2+} (Ca^{2+} 100 pm, La^{3+} 103.1 pm) ^[6]; however, under most biogeochemical relevant conditions, all REE form trivalent cations with the exception of Cerium (Ce), which also can exist in the tetravalent state, and Europium (Eu), which also can exist in the divalent state ^{[7][8]}. Thus, REE strongly interact with phosphate and negatively charged surfaces ^{[9][10][11]}, and their biogeochemical behavior resembles that of other trivalent metals, particularly Al^{3+} ^{[12][13][14]}. Consequently, REE can be used to model the geochemical behavior and speciation of trivalent actinides (Am^{3+} , Cm^{3+} , Cf^{3+}) in natural waters to predict their fate and transport ^[15].

All REE have the same outer electron configuration and show very similar chemical behavior ^[16]. The ground-state electronic configuration of La is the xenon core plus 5d1 and 6s1. After La, the 4f orbitals are filled, leading to an increasing contraction of the 5s and 5p electron orbits with increasing atomic number (the so-called lanthanide contraction). Thus, the effective ionic radius of the trivalent ions decreases slightly but systematically from La^{3+} (103.1 pm) to Lu^{3+} (86.1 pm) ^[7]. The radius of Ho (90 pm) is similar to that of Y ^[5]. Accordingly, REE are sometimes sub-grouped into light rare earth elements (LREE), including those with a lower mean atomic mass than 153 and a larger effective radius than 95 pm (La, Ce, Pr, Nd, Sm, and Eu) and heavy rare earth elements (HREE) including those with a higher mean atomic mass than 153 and a lower effective ion radius than 95 pm (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) ^[5]. Most of the

dissimilarities that do exist among REE in terms of the formation of Ce and Eu anomalies, as well as fractionation patterns, can be attributed to differences in their ionic radii or variations in valences (e.g., Ce³⁺ or Ce⁴⁺). In particular, the stability of complexes with electronegative organic and inorganic ligands, as well as sorption on surfaces, increases with decreasing ionic radius. Thus, in environmental compartments, the mobility of HREE often appears higher than that of LREE in the presence of ligands, whereas sorption processes preferentially immobilize HREE rather than LREE. As a result, individual REE can be enriched or depleted relative to other representatives of this group. Fractionation of HREE relative to the LREE has been reported during an array of biogeochemical processes ^{[17][18][19]}, justifying the use of REE as tracers (pseudo-isotopes) to investigate petro- and pedogenesis (e.g., ^{[20][21][22][23]}). In archaeology, the pattern of REE was successfully used to discern between natural and anthropogenic sediment units of paleosols, and REE signatures may help to assign fossils to their proper depositional unit ^[24]. In other research fields, the group of REE has been paid much less interest compared to the transition metals and metalloids, primarily due to the fact that REE has been neither considered essential nor strongly toxic to most biota. Thus, they were commonly neglected in plant nutrition and environmental sciences. However, in recent years, the number of publications on REE has rapidly increased due to their great importance for modern industry ^[25], which led to the intensification of mining and raised concerns about their environmental impact ^[26]. In particular, pollution of soils and water bodies with REE gave cause for concerns about their toxicity to plants, animals and humans, the fate of REE in soil–plant systems, REE cycling in ecosystems, and the impacts of REE pollution on food security ^{[9][27][28][29][30][31][32][33][34]}.

2. REE in the Lithosphere

2.1. Crustal Abundance and Geology

As lithophilic elements with a ubiquitous distribution in Earth's crust, the mineral distribution of REE tends to be controlled by silicate minerals, which are associated with 43% of all REE, followed by carbonates (23% of all REE), oxides (14%), and phosphates (14%) ^[35]. The average abundance of REE in the Earth's crust is typically higher for LREE than for HREE and varies from 66 mg/kg in Ce to 40 mg/kg in Nd and 35 mg/kg in La to 0.5 mg/kg ^{[3][4]}. LREE are primarily concentrated in late-stage felsic differentiates of the magma. In contrast, HREE are concentrated in the early-formed mafic products. Since the continental crust is composed mainly of granitic rocks, the crust is strongly enriched in LREE, together with K, Rb, Cs, Sr, Ba, Zr, Hf, Nb, Ta, W, Th, and U ^[36]. Igneous intrusions, notably carbonatic alkalic or peralkaline intrusions and pegmatites, contain significant concentrations of REE that occur as oxides, halides, carbonates, phosphates, and silicates but not as sulfides ^[37]. Of the 250 REE-containing minerals, only the REE phosphates bastnaesite (Ce, La, Nd, Y)[(F, OH)CO₃], monazite (La, Ce, Nd)PO₄, and xenotime (Y, Yb)PO₄ are located worldwide with usually large deposits, but they are present only in a few countries ^[38]. Apatites Ca₅(PO₄)₃(F,Cl,OH) may also contain considerable amounts of REE ^{[39][40]}. Within the group of silicates, REE are particularly contained in minerals from the epidote group ^[41] and zircon ^[42] ^[43] but have low concentrations in quartz. Large ionic radii and a high oxidation number make the REE incompatible with the crystal lattices of common minerals forming igneous rocks except Eu²⁺, which easily replaces Ca²⁺ in the structure of plagioclase. Following their distribution in rock-forming minerals, pegmatites, rhyolites, granites, and their metamorphic equivalents typically contain higher REE concentrations than basalts and peridotites (**Table 1**). Clays and shales typically have higher REE concentrations than limestones and sandstones ^[22]. However, some tholeiitic basalts within the Tertiary newer volcanic province of Victoria (South Australia) show anomalously high REE concentrations, which has been attributed to incipient alteration of the mineral composition of trace metal concentrations at the earliest stages of weathering ^[44].

Table 1. Occurrence of REE in different rocks (mg/kg). The median of 19 representative rocks from the Monchegorsk massif ^[45], grey granite from South Africa ^[46], and Cappadocia/Turkey ^[47].

Element	Monchegorsk	Granite	Limestone	Calcrete	Diatomite	Ignimbrite
Y	3.43	n.a.	2.9	15.2	20.2	14.7
La	2.81	22.2	3.5	19.8	30.8	32.1
Ce	6.48	55.7	4.9	31.5	52.8	52.7
Pr	0.80	6.5	0.6	3.9	6.73	4.43
Nd	3.46	25.2	3.1	14.5	25.5	14.5
Sm	0.67	5.6	0.5	2.4	4.23	2.41
Eu	0.30	0.7	0.1	0.6	0.93	0.43

Element	Monchegorsk	Granite	Limestone	Calcrete	Diatomite	Ignimbrite
Gd	0.68	4.7	0.6	2.3	3.77	2.02
Tb	0.11	0.7	0.1	0.4	0.61	n.a.
Dy	0.68	3.8	0.6	2.3	3.36	2.05
Ho	0.14	0.7	0.2	0.5	0.67	0.50
Er	0.36	1.7	0.4	1.5	2.03	1.53
Tm	0.05	0.2	0.1	0.2	0.28	0.40
Yb	0.33	1.4	0.4	1.6	2.12	1.74
Lu	0.05	0.2	0.1	0.2	0.32	0.28

n.a. = not available.

For the interpretation of geochemical and biological processes, REE concentrations found in rocks, soils, and even biological samples are often interpreted relative to concentrations in chondrites, like the chondrite Allende CV3 [48], the chondritic meteorite Leedy [49], or the post-Archean Australian shale [50]. Moreover, normalization approaches are frequently used to distinguish anthropogenic and background contributions, as seen in [51]. Normalization of REE concentrations compares the analyzed contents of single elements with a standard natural reference system, which facilitates the interpretations of rare element contents concerning fractionation, grouping, anomalies, and anthropogenic components. Chondrite has been used as a representative of the initial REE concentrations at formation time of the Earth's crust and shale as a representative of the post-Archean upper continental crust and reflects sedimentation geochemical processes [51]. The Post-Archean Australian Shale has been based on a set of nine Australian shale samples. The North American Shale Composite relies on 40 shale samples, of which 20 come from the US. The European Shale dates back to a Phanerozoic shale composite prepared in 1935. Mud from Queensland is based on unconsolidated fine-grained sediments [52]. Possibly, the different continents have different scales of original unweathered composition [46] [53], but the datasets are relatively close, as shale and its fine-grained precursor sediment are relatively homogenous erosion products, integrating a large area of the upper crustal material (**Table 2**). Versus chondrite, the standard shale shows equal proportions for elements from Eu to Lu throughout, but enrichments for La > Ce > Pr > Nd > Sm. Despite slightly different values, normalization versus different reference datasets does not alter interpretations and conclusions of given analytical data [52]. Whereas the shale datasets are similar, representing the continental crust, the reference for the mid-ocean ridge basalt is lower for LREE (La to Sm). Anomalies for specific elements can be quantified by linear extrapolation, interpolations using neighboring elements, or by geometric extrapolation using logarithmic modeling [51]. Cerium negative anomalies are characteristic for seawater because, under oxic conditions, Ce can be easily oxidized to the tetravalent state on the surface of Mn-oxides and thus co-precipitated. For calculation of this anomaly, interpolation from La and Pr or La and Nd and extrapolations from Pr and Nd have been used [51]. The calculation of Eu anomalies by interpolation from Sm and Gd can be interfered by Gd pollution from Gd inputs, which is used as a contrast agent in magnetic resonance imaging for medical purposes; thus, interpolation from Sm and Tb can be used instead.

Table 2. Normalization concentrations (mg/kg dw) [52] and mean crustal abundance [54].

Element (mg/kg)	Post-Archean Australian Shale	North American Shale Composite	Mud from Queensland	European Shale	Upper Crust	Lower Crust
Y	27.3	27	31.8	31.9	20.7	27.2
La	44.6	32	32.5	44.3	32.3	26.8
Ce	88.2	73	71.1	88.5	65.7	53.1
Pr	10.1	7.9	8.5	10.6	6.3	7.4
Nd	37.3	33	32.9	39.5	25.9	28.9
Sm	6.88	5.7	6.88	7.30	4.7	6.0
Eu	1.21	1.24	1.57	1.48	0.95	1.6
Gd	6.04	5.2	6.36	6.34	2.8	5.4
Tb	0.89	0.85	0.99	0.94	0.50	0.81

Element (mg/kg)	Post-Archean Australian Shale	North American Shale Composite	Mud from Queensland	European Shale	Upper Crust	Lower Crust
Dy	5.32	5.8	5.89	5.86	2.9	4.7
Ho	1.05	1.04	1.22	1.17	0.62	0.99
Er	3.07	3.4	3.37	3.43	n.a.	n.a.
Tm	0.45	0.5	0.51	0.49	n.a.	n.a.
Yb	3.01	3.1	3.25	3.26	1.5	2.5
Lu	0.44	0.48	0.49	0.49	0.27	0.43

n.a. = not available.

In the Monchegorsk ultramafic complex in the Kola region (Russia), some ultramafic rocks follow a nearly chondritic REE pattern, whereas others have a strong LREE enrichment (**Table 1**). Here, the main factor responsible for the REE distribution is their content in plagioclase ^[45]. In the region around Lake Baikal (Siberia, Russia), gneisses and mafic granulites show flat, normalized rare earth element patterns and moderate depletion of LREE, which are also reflected in the drainage waters. On the contrary, Paleoproterozoic volcanic rocks, which are felsic and rich in alkalis, have slight LREE enrichment and a prominent negative Eu anomaly ^[55]. Very detailed data on various lithofacies of Cappadocia (Turkey) has been given in ^[47], of which the most characteristic is summarized in **Table 1**.

In Austria ^[56] and Slovakia ^[57], geochemical inventories had been made and mapped based on grid-sampling of stream sediments of one sampling point per km². In Austria, median total Ce was 100 mg/kg and La 50 mg/kg; elevated levels were only found in the old crystalline of the Bohemian Massive. For Slovakia, details are given in **Table 3**.

Table 3. Results of geochemical inventories in Slovakia (mg/kg), median, and range.

	Ce		La	
	Median	Range	Median	Range
Andesites	50	20–88	28	11–61
Basic metavolcanites	24	5–60	15	2–39
Acid metavolcanites	60	14–123	34	9–89
Metapelites	70	29–126	41	10–71
Granites	62	10–147	33	1–83
Carbonates paleozoic	<10	<10–40	3	1–17
Carbonates mesozoic	20	<10–60	20	2–60
Clays	55	17–93	37	18–48
Sandstones	36	5–71	25	8–44

2.2. Sediments

2.2.1. Stream Sediments

The strong partition of REE into the particulate phase, their coherent behavior during weathering, erosion and fluvial transportation, and their high resistance to mobilization make REE in sediments a provenance indicator in geochemical studies. In sediment profiles, REE do not show enhanced fluxes from the bottom to the top ^[24]. Thus, sediments represent the temporally integrated state of a water body and depend on geological setting, weathering intensity, and erosion, and can be used as screens for pollution. The local concentration depends both on the local lithological composition and the transportation and sedimentation, as REE are enriched in minerals of high specific weight, in the fraction of the smallest grain size sieved, and deposited preferably close to barriers downstream.

The catchment of the Rhine covers possible REE inputs for a long time (**Table 4**). When REE concentrations in sediments of the Rhine were investigated ^[58], a high accumulation of LREE but not of HREE together with the common legacy pollutants (Ni, Cu, Zn, Cd, Pb) was found, particularly downstream of Cologne along the Lower Rhine, indicating

anthropogenically driven inputs of La and Sm from catalyst production and Gd inputs from municipal wastewater discharges. Similarly, in the sediments of Rio Tinto and Rio Oriel, which merge with the Atlantic Ocean in a typical estuary near the Gulf of Cadiz (Spain), [59] found substantial enrichment of Cu and rare earth elements (REE) in the cores as a consequence of former Cu mining and a fertilizer factory, which emitted Cu and REE. The REE concentrations in the estuary water were 1000 times higher than the ambient levels [59]. Compared to that, in the Chinese rivers, the Yangtze, the Yellow, the Sunhuajing, the Pearl, the Haihe, the Huahe, and the Liaohe, REE in sediments (<2 mm) rarely exceeded the crustal average (**Table 4**), although China has the majority of REE reserves in the world [29].

Table 4. Occurrence of REE in stream sediments of Aswan Lake [60], China's large rivers [29], the Vistula [61], the Rhine [58] and the Ganges [62]. Medians of total concentrations (mg/kg), except for Aswan. In addition to the median, the concentration range is given for rivers in China.

Element	Aswan Lake	China's Large Rivers	Vistula River	Rhine River		Ganges		
Location		n.a.	n.a.	upper	lower	main central	Porphyroids	Proterozoic
Fraction	Total, unsieved	HNO ₃ < 2 mm	Total < 0.02 mm	Total < 0.063 mm		Total < 0.18 mm		
Sc	25.7 ± 3.4	11.6 (1.32–23.1)	5.74	n.a.	n.a.	n.a.	n.a.	n.a.
Y	n.a.	14.6 (3.31–24.8)	12.7	n.a.	n.a.	n.a.	n.a.	n.a.
La	34.2 ± 6.5	31.1 (7.56–57.3)	19.4	29	72	86.1	40.5	30.2
Ce	81 ± 14	65.3 (16.5–123)	41.1	54	94	195	87.1	61.6
Pr	n.a.	7.57 (1.59–14.3)	4.79	6.2	10.5	n.a.	n.a.	n.a.
Nd	n.a.	29.3 (5.6–58.5)	18.9	23	39	46	28.2	26.8
Sm	8.7 ± 1.4	5.33 (1.09–11.0)	3.84	6.5	7.8	12.23	6.52	5.59
Eu	2.1 ± 0.5	0.87 (0.05–1.72)	0.82	1.17	1.29	1.86	1.41	1.40
Gd	n.a.	8.86 (1.64–16.8)	3.65	5.4	6.2	9.87	5.40	4.39
Tb	n.a.	0.65 (0.12–1.16)	0.51	0.75	0.76	1.68	0.93	0.75
Dy	n.a.	3.20 (0.53–4.96)	2.85	4.2	4.3	9.45	5.27	4.11
Ho	n.a.	0.57 (0.09–0.99)	0.50	0.79	0.81	1.88	1.05	0.80
Er	n.a.	1.40 (0.26–2.44)	1.29	2.18	2.26	5.77	3.07	2.32
Tm	n.a.	0.18 (0.06–0.38)	0.17	0.31	0.32	0.85	0.42	0.32
Yb	0.75 ± 0.14	0.96 (0.22–2.89)	1.03	2.00	2.12	5.05	2.38	1.84
Lu	0.45 ± 0.07	1.15 (<0.02–0.42)	0.15	0.28	0.31	0.77	0.34	0.27

n.a. = not available.

The geochemical survey of Austria covers the total composition of stream sediments (<0.18 mm), but the dataset had been restricted to La and Ce. The sediments are enriched in heavy minerals like monazite, bastnaesite, allanite, titanite, epidote, and apatite. The available datasets reveal concentration minima in limestone areas (La < 13 mg/kg and Ce < 24 mg/kg) and enrichment at the edges of crystalline rocks (La: 13–24 mg/kg, Ce: 24–45 mg/kg). Due to higher levels of REE in post-glacial sediments than limestones, La ranged within 25–55 mg/kg and Ce within 46–102 mg/kg [56]. In stream sediments of the Slovak Republic (<125 µm), Ce accumulated in the heavy mineral fraction with an average content of 61 ± 23 mg/kg. The 25 percentile was 50 mg/kg, the 75 percentile was 69 mg/kg, and the 99 percentile was 140 mg/kg. Here, concentrations below 48 mg/kg were typically found in Mesozoic carbonates and, to a lesser extent, Paleogene and Neogene sediments. In contrast, the above-average values were associated exclusively with crystalline units in the Tatra and the Paleozoic metamorphosed rocks of the Spišsko-gemerske ore mountains [57]. In the Campania region (Italy), stream sediments cover a wide range of geological facies, like alluvial sediments, volcano-sedimentary deposits, siliciclastic, and carbonate deposits, as well as limestones and dolostones. The median and range of 2389 stream sediments were 15.8 mg/kg for La (range 1.2–124.2) and 2.4 mg/kg for Sc (range 0.40–12.6) [63]. Similarly, sediment samples from small headwater streams to the Ganges in a remote area in the South-Western Himalaya (**Table 4**) reflect

distinct geologic characteristics of the area. The REE contents decrease from the highly metamorphosed rocks of granitic parentage of the Main Central Thrust Zone MCTC towards a zone of porphyroids and finally towards a zone of Proterozoic metasedimentary sequence [62]. Unsieved sediments of the Aswan High Dam Lake (Egypt-Sudan) contain Fe, Co, Sm, and Eu in relatively uniformly distributed amounts, whereas for Al, Sc, La, Ce, and Th, a distinct increase downstream was noted [60], which could be largely explained by the late sedimentation of REE-enriched fine particles such as clays. Conversely, the distribution of REE in sediments 10 km downstream the Vistula (<5 µm, 5–10 µm, and 10–20 µm) was explored, and decreasing concentrations of REE with decreasing particle size were found, which suggests that accessory minerals are more critical than clay minerals in controlling the rare earth element distribution in this river [61]. This highlights the importance of considering particle fractions during geochemical studies on sediments, allowing further interpretations of processes related to element transport and sequestration.

2.2.2. Marine Sediments

Compared to sediments of terrestrial water bodies, the literature on REE concentration patterns in marine sediments is scarce. Ferromanganese concretions at the bottom of the seas are classified into hydrogenous, oxic-diagenetic, suboxic-diagenetic, and hydrothermal varieties due to their origin. The hydrogenous-type concretions (vernadite δ -MnO₂) occur as crusts on seamounts and are enriched in Fe, Co, and REE, particularly in Ce, whereas the abundance of REE in other types of deep-sea nodules is low. Versus mean crust values, the enrichment is maximum for Sm and decreases from Sm down to La and Sm up to Lu. The contents of REE in oxic-diagenetic nodules are at the same levels as in associated siliceous sediments [64]. In carbonate-dominated marine sediments, REE remain preserved and permit conclusions about the oxygenation during the sedimentation period. Hydrothermal fluid inflow causes a positive Eu anomaly, and well-oxygenated seawater leads to a negative Ce anomaly [65].

2.3. Coal and Coal Ash

REE concentrations in coal typically do not exceed the average crust concentration; however, lignite and peat often appear enriched in REE (Table 5). In coal from Saxony/Germany, REE occur in small, well-distributed Al minerals or are adsorbed on their surface [66] (Vogt 1994). The distribution of minerals and major, minor, and trace elements within the lignite seams is often very different from distribution in the enclosing sediments and associated inorganic horizons. In particular, in Alabama coals, Ce was found to be consistently associated with minerals, while Sc-Y-Yb were at least partially associated with organic matter. Yb was higher in the inorganic horizon than in the organic, but taken as ash-based data, the concentrations were higher in the organics [67]. Ce, Dy, Eu, La, Nd, Tb, and Yb were determined in brown coal and lignite used in Austria and the resulting bottom ash and fly ash [68]. Based on the dataset given by Wedepohl [54] for the continental crust, which allows the extrapolation of lacking elements, the sum of REE in the Austrian brown coals (75 samples) can be estimated at 94.5 mg/kg. The REE concentrations reached 107 mg/kg (25 samples) in imported hard coals from Poland and Australia. In bottom ash, REE were present with 223 mg/kg, and in fly ash with 243 mg/kg (Table 5), indicating a significant enrichment during combustion.

During coal combustion, REE are mainly concentrated in the coarse residues or at least equally partitioned between coarse residues and fine particles [69]. Alkaline fly ash samples from coal-fired thermal electric power plants contain ferromagnetic spherical particles and aluminosilicates. Most ferromagnetic fractions contain significant quantities of a spinel (magnetite, Fe₃O₄) and minor quantities of quartz, hematite, and magnetite. About 45% of the ferromagnetic fraction was leachable with 0.5 M HNO₃ and contained total REE concentrations similar to standard magnetite as an exterior coating of thin shells on fresh ferromagnetic particles [70]. REE minerals remain unchanged during coal combustion (below 1500 °C). In the slag, elemental mapping by EDAX (energy dispersive X-ray spectrometry) showed that the Al and P distribution still coincides with those of La, Ce, and Nd but not with Si. In addition, in the corresponding aluminosilicates, correlations between Al and the REE were much more pronounced than between Si and the REE [71]. In coal fly ash, most of the REE are dispersed in the Al-silicates glassy matrix, which impairs REE recovery through leaching [71][72]. Calcination pretreatment can increase their recovery substantially due to the removal of the organic matter, as demonstrated for coals of the Fire Clay and Western Kentucky seams that contained 502–1968 mg/kg of total REE, mainly as phosphate minerals like monazite [72].

Table 5. REE (mg/kg) in coal and coal ash (mean ± sd or median and range).

Element	East Alabama	West Alabama	Darco	Wall	Lignites *	Hard Coal *	Bottom Ash	Fly Ash	Argonne Coal	Argonne Coal Ash
Reference		[67]					[68]		[73]	[74]

Element	East Alabama	West Alabama	Darco	Wall	Lignites *	Hard Coal *	Bottom Ash	Fly Ash	Argonne Coal	Argonne Coal Ash
Sc	3 (2–5)	2 (0.7–5)	3 (0.8–8)	1 (0.7–3)	6.6 ± 3.4	4.2 ± 3.3	16.2 ± 6.1	16.4 ± 8.1	2.18 (0.81–7.61)	20 (9.4–33)
Y	9 (7–11)	13 (7–21)	6 (3–13)	5 (2–10)	10 ± 7	9.6 ± 3.5	40.3 ± 16.6	46.3 ± 14.9	n.a.	39 (25–86)
La	14 (9–17)	3 (2–7)	5 (0.7–12)	5 (1–14)	18 ± 9	16.7 ± 12.2	42 ± 26	44 ± 18	6.1 (2.8–21.5)	64 (39–137)
Ce	n.a.	n.a.	n.a.	n.a.	30 ± 15	25.8 ± 23.1	84 ± 36	92 ± 28	11.4 (4.4–30)	n.a.
Nd	n.a.	n.a.	n.a.	n.a.	29 ± 15	42.5 ± 38.0	49 ± 33	62 ± 1	8 (2.3–11.9)	77 (39–113)
Sm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.14 (0.41–3.52)	8.1 (<3–14)
Eu	n.a.	n.a.	n.a.	n.a.	0.6 ± 0.3	0.43 ± 0.42	1.18 ± 0.63	1.15 ± 0.53	0.22 (0.08–0.67)	n.a.
Tb	n.a.	n.a.	n.a.	n.a.	0.6 ± 0.2	0.71 ± 0.52	1.19 ± 0.55	1.13 ± 0.48	0.14 (0.06–0.40)	n.a.
Dy	n.a.	n.a.	n.a.	n.a.	2.9 ± 1.7	2.43 ± 1.81	3.9 ± 2.5	3.1 ± 2.0	n.a.	5.5 (2.0–9.2)
Yb	0.8 (0.5–1.2)	2.6 (2–4)	0.6 (0.3–1.1)	0.3 (0.1–0.8)	1.6 ± 0.7	2.05 ± 1.43	1.56 ± 0.73	2.05 ± 1.43	0.50 (0.20–1.6)	n.a.
Lu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	16.2 ± 6.1	16.4 ± 8.1	0.13(0.04–0.22)	n.a.

* Lignites and hard coal used in Austria in 1988; n.a. = data not available.

3. Pedosphere

3.1. Occurrence in Soil

The concentrations of REE in soils depend on the soil parent material, climate, time, and biological activity determining soil genesis, weathering intensity, and consequently mobility and sequestration of REE in/on secondary minerals and soil organic matter [75][76][77][78][79]. Given that soils are composed of heterogeneously distributed primary and secondary mineral phases and organic compounds, soil REE signatures are an amalgamation of the signatures belonging to each mineral group. This might explain why the median level of REE in Chinese soils is not higher than elsewhere (177 mg/kg REE) and ranged from 85 to 523 mg/kg but with some hotspots with LREE enrichment [18][80]. Many soil-forming processes cause dramatic losses of REE; consequently, soils typically show lower concentrations than the parent material from which they are derived (**Table 6**). REE concentrations in soil reflect weathering intensity rather than rock type, given that observed differences in soil REE concentrations can rarely be related to variations in bedrock. Chemical weathering of the host rocks drives the dissolution of the primary REE-bearing minerals [79]. The mobilized REE either co-precipitate in secondary minerals, sorb to appropriate surfaces, or leach into adjacent water bodies. Secondary minerals formed during silicate weathering may absorb and concentrate the REE liberated from primary minerals [81][82]. Thus, excessive REE losses are typically related to intensive weathering of both primary and secondary mineral phases. The literature indicates that soils developed upon felsic rocks such as granite, gneiss, and quartz rocks, at least tend to contain higher concentrations of REE, especially LREE, than soils derived from mafic rocks (basalt), which tend to contain lower total REE concentrations but may be relatively enriched with HREE [76][77][83]. However, soils developed on tholeiitic basalts within the Tertiary newer volcanic province of Victoria (South Australia) showed anomalously high REE concentrations, which has been attributed to REE released during the earliest stages of weathering and subsequent sequestration in secondary phosphate or clay minerals [44]. Decreasing soil REE concentrations have been reported in the order basalt > clay slate > loess > sandstone, which can be largely explained by an increasing portion of REE-depleted quartz [84][85]. In underdeveloped lithosols of the Ditrau Alkaline Massif in the Eastern Carpathian Mountains, characterized by an intrusion body within pre-Alpine metamorphic rocks formed by nepheline syenite, syenite, and mazonite, Ion [86] found

extraordinarily high concentrations of total REE (median 273 mg/kg). On the contrary, in highly weathered lateritic soils, the upper ferruginous horizons appeared significantly depleted in REE, but also showed distinct accumulation zones of REE, especially in the basal saprolite [79][87]. When the characteristics of Australian soil derived from the weathering of the Toorongo Granodiorite were investigated, lower concentrations in soil than in the parent granodiorite were found, but REE enrichment in zones of intermediate weathering, highlighting the influence of weathering conditions on the content of REE in the soil [88]. Given that the mobility of REE in soils does not depend on dissolution and sorption processes only, but also on complexation and ligand exchange reactions [89], the presence of ligands often explains differences in the concentrations of total REE along soil profiles as well as the pattern of LREE and HREE [82]. In Japan, the highest total REE contents were found in red soils [76][77]. Andosols with elevated carbon and phosphate levels exhibited intermediate total REE but were enriched in heavy rare earth elements (HREE). Conversely, highly weathered Acrisols, which were also depleted in numerous soil cations and phosphate, displayed the lowest total REE concentrations (**Table 6**). Similarly, acidic spodosols and podzols are characterized by the downward migration of REE together with Al and Fe as organic complexes [39][90][91]. In podzols of cold temperate regions of Sweden, the loss in the eluvial E-horizon was significantly higher for LREE (80–85% of La) than for HREE (54–60% of Yb) and the B-horizons appeared to be enriched through REE reabsorption on secondary oxy-hydroxides, clay minerals and organic material. In contrast, higher losses of HREE relative to LREE reported in soils across different tropical and temperate soils [46][82][92] are typically related to the presence of carbonates and the higher affinity of HREE to form stable aqueous complexes [82]. During weathering in a semi-arid Mediterranean climate (Cape Province, South Africa), the increase in REE with depth reflected the change from the acidic organic-rich upper layer to alkaline carbonate precipitates at deeper layers [46]. Similarly, high concentrations of REE in soils near reefs, with their high carbonate and organic carbon contents, are typically caused by REE co-precipitation with marine carbonates or scavenging with particulate organic matter [93]. In Germany, soils developed from loess had higher REE levels than soils derived from Pleistocene and Holocene sediments or organic material [94]. The aqua regia extractable REE correlated significantly positively with clay contents, cation exchange capacity, and soil pH but negatively with organic carbon, according to [94]. Possibly, differences in other physicochemical properties related to the bedrock impacted soil REE concentrations more strongly than differences in organic matter contents, or a higher carbon content fostered the leaching of REE. In contrast, Wiche et al. [95] found a positive relationship between soil organic matter and total REE contents in various soil types derived from the same parent material (gneisses). The researchers emphasize that soil organic matter has a dual role in REE sequestration and leaching. A higher content of particulate organic matter may contribute to REE sequestration and accumulation in a given soil, whereas dissolved organic carbon favors the leaching of REE [89][96].

Table 6. Median concentrations and ranges (mg/kg dw) of total REE in the continental crust, Baltic soils, 25 agricultural soils of Sweden, 24 soils from apple orchards in Austria, 843 soils of Europe, topsoils in China and Japan, 43 soils of Parana state Brazil, and lateritic soils of east Cameroon.

Element	Earth Crust ^{1,2}	World Soil Average ³	Baltic Soils ⁴	Topsoils Sweden ⁵	Topsoils Austria ⁶	Soils of Europe ⁷	China ⁸	Andosols Japan ⁹	Cambisols Japan ⁹	Acrisols Japan ⁹	Soils of Brazil ¹⁰	Lateritic Soils Cameroon ¹¹
Sc	14	11.7	n.a.	n.a.	12 (7–18)	9.1 ± 5.6	n.a.	28 (10–51)	17 (7–41)	13 (2–37)	31 ± 15	n.a.
Y	31	33.0	n.a.	4.9–17.6	23 (15–34)	n.a.	n.a.	24 (12–72)	16 (7–67)	9 (3–28)	28 ± 8	17 ± 10
La	35	27	33 (2.3–113)	5.5–33.2	47 (30–69)	26 ± 16	35 (7–184)	19 (3.8–51)	23 (10–120)	21 (4–55)	38 ± 14	12 ± 6
Ce	66	56.7	37 (3.7–167)	11–68	58 (43–79)	52 ± 31	75 (16–454)	42 (10–100)	66 (2–140)	58 (7–150)	96 ± 38	23 ± 13
Pr	9.1	7.0	4.3 (0.4–24)	1.3–7.5	5.5 (3.8–12.5)	6.3 ± 3.6	n.a.	4.8 (1.1–11)	5.0 (2–31)	4.1 (0.7–9.9)	9.1 ± 3.4	2.6 ± 1.5
Nd	40	26	16 (1.7–86)	9.3–53	20.6(14.5–47)	22 ± 14	33 (7.6–62)	22 (6–45)	20 (8–120)	15 (3–36)	34 ± 13	9.9 ± 6.0
Sm	7.0	4.6	3.0 (<0.2–15)	0.9–4.6	3.9 (2.9–8.6)	4.3 ± 2.6	5.6 (1.6–26)	4.6 (1.4–9.7)	4.1 (1.4–26)	2.8 (0.4–5.9)	6.9 ± 2.7	1.9 ± 1.0

Element	Earth Crust ^{1,2}	World Soil Average ³	Baltic Soils ⁴	Topsoils Sweden ⁵	Topsoils Austria ⁶	Soils of Europe ⁷	China ⁸	Andosols Japan ⁹	Cambisols Japan ⁹	Acrisols Japan ⁹	Soils of Brazil ¹⁰	Lateritic Soils Cameroon ¹¹
Eu	2.0	1.4	0.6 (0.06–2.3)	0.2–0.8	0.9 (0.6–1.2)	0.9 ± 0.5	1.1 (0.2–7.0)	1.3 (0.7–2.2)	1.2 (0.6–8.1)	0.8 (0.2–1.3)	1.6 ± 0.7	1.2 ± 0.3
Gd	6.1	3.9	2.8 (0.24–13)	1.0–4.8	3.7 (2.6–5.4)	4.2 ± 2.7	n.a.	4.7 (1.6–9.5)	3.7 (1.4–22)	2.1 (0.5–5.9)	5.7 ± 2.3	1.7 ± 0.7
Tb	1.2	0.63	0.4 (<0.05–2.0)	0.15–0.65	0.5 (0.4–0.8)	0.6 ± 0.4	0.77 (0.2–2.7)	0.8 (0.3–1.4)	0.7 (0.3–3.0)	0.4 (0.1–1.0)	1.0 ± 0.4	0.3 ± 0.1
Dy	4.5	3.6	2.3 (0.24–10)	0.90–3.76	n.a.	3.6 ± 2.4	n.a.	4.5 (1.7–9.4)	3.3 (1.4–15)	1.5 (0.5–5.0)	5.7 ± 2.2	2.5 ± 0.9
Ho	1.3	0.72	0.4 (0.05–2.0)	0.20–0.74	0.5 (0.3–0.7)	0.7 ± 0.5	n.a.	0.8 (0.4–1.7)	0.6 (0.3–2.4)	0.3 (0.1–0.9)	1.1 ± 0.3	0.7 ± 0.4
Er	4.9	2.2	1.3 (<0.15–5.0)	0.63–2.2	1.3 (0.9–2.0)	2.1 ± 1.4	n.a.	2.5 (1.1–5.9)	1.7 (0.8–5.7)	1.0 (0.4–2.9)	3.2 ± 1.1	1.9 ± 1.4

3.2. Mobility and Speciation in Soil

Despite the relatively high REE concentrations in soil (Table 6), under most pedological conditions, their mobility is low (Table 2). The mobility of REE in soils is a function of their ionic radii and speciation in solution, pH, Eh, water fluxes, and the nature of secondary intermediate minerals formed under different conditions. Sorption of clay minerals, phosphates, Fe-/Mn-hydroxides, Al hydroxides, and soil organic matter (SOM) decrease the solubility and mobility of REE in soils. Conversely, the presence of inorganic and organic ligands such as sulfate, carbonate, oxides, carboxylates, humic and fulvic acids can counteract sorption and foster their presence in the soil solution. However, there is also evidence that REE(III)-humate may bind on the surfaces of Fe-/Mn-oxyhydroxides, lowering its abundance in soil solution. Dong et al. [121] estimated that of the total REE in soil, 1.8–26.5% of REE are bound into soil organic matter. Although REE sorbed onto mineral surfaces represent a relatively small element pool in soil [112], this pool is susceptible to slight physical-chemical changes and can contribute significantly to the mobility of REE in soil. Based on the point of zero charge (pzc) of various minerals, it was concluded that REE sorption is mainly controlled by the pH range (pH 4–5), whereas carbonate, hydroxide, and oxide minerals are predominant in circumneutral to slightly acidic pH ranges, and in strongly acidic soils (pH 2–5) REE sorption onto manganese oxides becomes increasingly important [123].

The concentrations of REE in soil solution typically lie between 0.1 and 0.5 µg/L for a single element and rarely exceed 1 µg/L for the sum of all REE [116][125]. At comparable DOC concentrations in soil solutions, REE mobility in soil is inversely related to soil pH [126][127]. Fluctuations in soil water contents may locally change the redox potential and pH of soils, thus strongly affecting the mobility and speciation of REE [114]. In the soil solution, REE can occur in a variety of chemical forms, such as ions [16], dissolved complexes [108], and colloidal forms [89][114]. In wetland soil solution or shallow groundwater, ultrafiltration shows that REE are mainly concentrated in the high-molecular-weight fraction and the colloid phases, which consist of Fe and organic matter. Soil organic matter has many negatively charged groups per unit dry weight, and a high capacity to adsorb or chelate divalent and trivalent cations. In soil systems rich in organic matter, about 46–74% of REE mobility in soils derives from the interactions with humic compounds [125] but strongly varies depending on pH, redox conditions, type, contents, and composition of the organic compounds [128][129].

Davranche et al. [114] demonstrated that REE are released from wetland soils mostly bound to colloidal organic matter related to the organic matter desorption caused by the rise in pH imposed by the reducing reactions during the flood season. The stability of REE-(Tb, Yb, and Gd)-complexes with humic substances may be especially high in neutral to moderately alkaline (pH 8–9) conditions [121]. The stability of HREE with most inorganic and organic ligands typically increases with increasing atomic number and consequently decreasing atomic radius [130], leading to a fractionation of HREE in soils relative to LREE. Given that HREE form more stable complexes with many soil constituents than LREE do [131][132][133], SOM often appears to be enriched in HREE relative to LREE [39][133][134]. Ma et al. [135] observed a strong positive Ce-anomaly in REE patterns of organic matter, probably because complexation capacities and formation constants of humic acids are higher with Ce than with the other LREE [136]. In podzols, the percentage of total REE in

general, and especially of HREE bound to organic matter, increases with soil depth [39][134] due either to the preferential complexation or the migration of HREE-complexes [39][134].

4. REE in the Hydrosphere

4.1. Speciation in Solution

The concentrations and speciations of REE predominantly depend on processes at the water/rock or water/soil interface governed by the physicochemical parameters of the water and the composition of soil/rock [5][108][137][138][139][140][141][142][143][144][145][146][147][148][149][150][151][152]. Truly dissolved REE typically represent a minor fraction of REE in the solution [89][114] because free REE^{3+} ions strongly interact with oxides or they are attracted to sorption surfaces, especially oxides and organic matter [113][124][148][153]. Under most physiologically relevant pH conditions (pH 5–7), REE show weak hydrolysis [154], and their solubility and chemical speciation are governed by complex formation with PO_4^{3-} , CO_3^{2-} , SO_4^{2-} , Cl^- , and F^- [155], where REE compete with other cations depending on ionic strength and pH [39][154]. At 3.5% salinity, it was found [156] that REE preferentially form complexes with carbonates but with slight differences between LREE and HREE. Lanthanum preferentially (86%) occurred in the form of MCO_3^+ and MCO_3^{2-} , 7% was present in free ionic form, and 7% was bound as hydroxide/sulfate/chloride/fluorides. In contrast, only 0.5% of Lu remained uncomplexed, 96% was present as dissolved carbonate species, and 1.5% formed hydroxide, sulfate, chloride and fluoride complexes. Accordingly, in groundwater with low Nd concentrations (0.22–0.80 ng/L), high pH (pH 6.9–8.6) and low DOC contents (0.08–0.15 mg/L) speciation modeling revealed that NdCO_3^+ and $\text{Nd}(\text{CO}_3)_2^-$ accounted for the majority of dissolved Nd (70–92%). In contrast, the species NdOH^{2+} , NdCl^{2+} , NdF^{2+} , NdSO_4^+ and NdHPO_4^+ were found to be negligible [108]. Yttrium and Ho have similar ionic radii and charge, but in an aqueous solution, Y–Ho fractionation takes place by preferential Ho-scavenging onto Fe-oxyhydroxides relative to Y as well as the preferential incorporation of Ho into CaCO_3 [157]. The higher stability of HREE carbonate complexes compared to complexes with LREE explains the HREE enrichment in hypersaline groundwaters in Australia, while in seawater and most other natural waters, the concentrations of REE typically decrease with increasing atomic number with respect to average shale [89][108]. Given that the complex stabilities of REE with organic compounds are much higher than with inorganic ligands, the chemical speciation of REE is strongly influenced by DOC and POC [156], determining the element's distribution between dissolved and colloidal forms. Many ultrafiltration studies demonstrated that REE in the dissolved fraction occur as colloid-borne particles [138][140][141][147][149][158][159][160][161]. In arctic glacial meltwaters and glacial-fed river waters from Western Greenland, the truly dissolved amount of REE obtained after ultrafiltration of 10 kDa was just 1/1000 of the total [162]. There is broad evidence that humic/fulvic acids act as carrier phases of dissolved REE [89][149][163][164][165][166][167]. For humic acids, increasing REE binding from pH 2 to pH 10.5 was demonstrated [89], similar to the complexation of REE with acetic acid, thus suggesting carboxylic groups with low pKa (pKa 5–6) as the primary binding sites. However, bidentate complexation with phenolic groups (with higher pKa > 8) cannot be completely ruled out [89]. The stability of REE complexes with humic substances is exceptionally high at moderately alkaline (pH 8–9) conditions [121]. However, more than 95% of the REE present in river water acidified to pH 3 was found in their complexed form with organic compounds [143], indicating that related complexes may occur over a wide range of biogeological relevant pH conditions, depending on the composition of DOC and consequently the prevailing functional groups. The binding of polydentate ligands is entropically favored compared to that of monodentate ligands. Simple carboxylic acid groups tend to form weaker monodentate complexes in environments with high REE concentrations, whereas multidentate complexation might be more relevant when REE concentrations are low [165]. In particular, enrichment of middle mass REE seems to be associated with the monodentate complexation, while HREE enrichment may derive from complexation with stronger binding sites [165].

4.2. Limnic Water Bodies

The total REE abundances in water depend on the watershed limnology, stream hydrology, climate, groundwater, landscape, and anthropogenic impact [55]. Therefore, compared to their relatively equal distribution in the earth's crust, the concentration of REE in limnic water bodies varies by several orders of magnitudes. Typical ranges between 1 ng/L and a few hundred ng/L for a given element from this group (Table 7) depend on weathering, the source materials, and the removal during the formation of autogenic, biogenic, and inorganic solids such as carbonates and oxyhydroxides [153][157][168]. Acidic conditions may favor higher total REE concentrations [163]; however, the processes involved depend not solely on REE solubility but are often influenced by other biogeochemical processes solution-surface chemistry governed by pH in concert with Eh, TOC, and salinity [55][169]. In general, freshwater contains higher REE concentrations than seawater because in river water the REE are associated with inorganic nanoparticles and colloids [170]. [170] compared REE concentrations in freshwater and saltwater samples from Germany and the Netherlands and found 26–280 ng/L (total REE plus yttrium) in freshwater, whereas in saltwater, the concentrations rarely exceeded 10 ng/L. In the Canadian St. Lawrence River and the Athabasca River, less than 20% of REE were found to be present in dissolved forms [171]. At the

river mouth of the Amazonas, the concentrations of soluble Fe and REE rapidly decline with increasing salinity through the removal of dissolved Fe and co-precipitation of REE [140]. In the Karstic groundwater system of Guizhou (SW China), which is dominated by limestones and dolomites, the sum of dissolved REE was <0.15 µg/L (range 0.03–0.99 µg/L) [169]. In Lake Baikal, the sum of total REE varied from 0.02 to 2.16 µg/L as a function of season and year [55], and model calculations demonstrated that REE are predominantly present in the form of carbonate and humic complexes [172].

REE are commonly used as tracers for geochemical processes in natural water bodies. The normalized patterns of the abundance of the REE can be used to trace the origin of suspended matter in river waters [55], given that anomalies in water might be relatable to the source rocks of the watershed [158]. Based on $^{147}\text{Sm}/^{144}\text{Nd}$ ratios, the origin of Rhine water downstream of Basel could be identified [158]. Depletion of both LREE and HREE is typical for phosphate inputs; however, chemical weathering and sorption processes during element transport lead to extensive fractionation between river water's dissolved REE composition and river-suspended particles. Tropical rivers usually show MREE enrichment, whereas temperate rivers show enrichment of HREE (Table 7) and negative Ce-anomalies concerning chondritic normalization [162]. In the coagulation region of river colloids, more Ce is precipitated than La and Nd [140]. In addition, in oligotrophic and oxygenated river waters, negative Ce anomalies and positive Y anomalies may derive from Ce co-precipitation and oxidation on FeOOH and less sorption of Y than other REE onto particulate matter [158][173] governed by pH and DOC [169]. On the contrary, LREE often appear to be enriched in arctic lakes and rivers that usually do not develop positive Eu anomalies because processes of Eu reduction do not take place in low-temperature environments [162]. In the Karstic groundwater system of Guizhou (SW China), most river water samples exhibited enrichment of MREE and negative Eu and Ce anomalies, whereas the suspended matter and surface sediments showed positive Ce and Eu anomalies [169]. From volcanic ash, siderophore-promoted transfer of REE and Fe into glacial meltwater, river, and ocean water has been observed [174].

In addition to geochemical processes, REE fractionation patterns in water are significantly influenced by biological activity altering the physicochemical water properties and cycling of specific REE species from the water phase [175]. It was demonstrated [157] that phytoplankton liberates REE from Fe-rich particles and accumulates both Ce(III) and Ce(IV), which may counteract the formation of a Ce anomaly even under oxic conditions. In addition, anthropogenic inputs of REE with wastewater discharge may strongly alter REE signatures of stream waters, primarily through the medical application of Gd-chelates [52][158][162][170][176]. [177] investigated the fate of cerium dioxide (CeO_2) nanoparticles in municipal wastewater during activated sludge treatment.

Table 7. Concentrations of dissolved REE (ng/L) in water samples from tropical and temperate rivers compared with groundwater collected around Bergen and Oslo (Norway).

Source	Groundwater ¹	Mississippi ²	Sepik ²	Fly ²	Amazon ²	Amazon River Mouth ³	Luce ⁴	Fraser ⁴	Dordogne ⁴	Garonne ⁴	Columbia ⁴	Sacramento ⁴
Region	Norway	USA	New Guinea		South America	Guyana	Scotland	Canada	France		North America	USA
Y	110–130	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
La	46–57	3.9	38	35	40	47	192	97	48	47	30	8.1
Ce	8–13	7.3	85	81	111	118	451	155	77	81	58	11
Pr	1–8	1.4	13	12	n.a.	n.a.	n.a.	28	11	5.2	9.9	7.2
Nd	31–37	7.3	57	55	73	76	264	88	37	38	23	11
Sm	3–8	21	15	15	17	20	59	25	7.3	8.2	44	2.5
Eu	n.a.	0.7	4.4	3.3	4.1	4.9	15	7	1.3	1.6	1.6	1.0
Gd	6–9	3.6	17	17	19	22	58	53	0.8	8.8	6.5	5.1
Tb	1	0.5	2.3	1.9	n.a.	n.a.	n.a.	43	1.3	1.2	1.2	0.5
Dy	n.a.	4.5	13	11	22	19	43	n.a.	n.a.	n.a.	n.a.	n.a.
Ho	2–3	1.2	2.3	2.2	n.a.	n.a.	n.a.	7	1.2	1.6	0.9	0.4
Er	7–9	4.1	6.1	5.3	11	11	24	14	4.3	4.1	n.a.	n.a.
Tm	1–2	0.6	0.8	6.7	n.a.	n.a.	n.a.	n.a.	0.6	0.6	n.a.	n.a.

4.3. REE in Seawater

Source	Groundwater	Mississippi	Sepik	Fly	Amazon	Amazon River Mouth	Luce	Fraser	Dordogne	Garonne	Columbia	Sacramento
1	1.12	2.9	4.6	4.6	8.4	9.3	20	75	12.0	26	45	75

In seawater, the level of total REE steadily increases with depth, because they are transported to the sea floor by settling particles, which finally form nodules at the bottom. Thus, for 15–750 m depth, 12.0 ng/kg had been reported for the Pacific, and 14.7 ng/kg for the Atlantic Ocean, resp., for 100–3500 m depth 23.9 ng/kg for the Pacific, and 25.0 ng/kg for the Atlantic Ocean, and finally 30.6 ng/kg for the Atlantic deep-sea. Differences and uncertainties are mainly influenced by Ce oxidation/precipitation, which had been observed to be higher in the Pacific than in the Atlantic Ocean [64]. The carrier phase is probably biogenic amorphous silica or diatomae. In the interstitial water of the deep-sea sediments, the rare earth concentrations are lower than in the overlying bottom water. Hydrothermal solutions are strongly enriched in LREE relative to seawater and display a pronounced positive Eu-anomaly [8], which is also evident in hydrothermal iron oxide crusts.

Nevertheless, with respect to mean crust abundances, the seawater is enriched in HREE and depleted in LREE because of the complexation with organic and inorganic ligands [140]. The main species in oxygenated seawater are carbonate complexes. The stability of carbonate and lactate complexes and the hydrolysis constants of the REE increase almost monotonically from La to Lu [64]. During flood periods, reducing conditions and a rise in pH causes a mobilization of REE from their particulate phase, which mainly consists of dead or living organic matter. Bacteria, diatomae cells, and algae cell surfaces represent significant binding sites for REE due to the prevailing carboxylic and amino functional groups [179]. Thus, thin organic coatings strongly affect the adsorption behavior of suspended particles in seawater, similar to limnic water bodies. Given that the monocarboxylate complexation constants substantially increase from LREE to HREE, the formation of soluble REE-carboxylate complexes might explain the enrichment of HREE in seawater [179].

4.4. Groundwater

The concentration of REE (sum of La–Lu) in groundwater rarely exceeds a few µg/L and typically ranges between 1 and 100 ng/L for specific representatives of this group [81][178]. Water samples from Norwegian bedrock groundwater boreholes drilled in Paleozoic and Precambrian igneous or metamorphic aquifers (pH range 7.22–8.95) contained a sum of dissolved REE concentrations of about 162 µg/L [180], which could be largely explained by the geological setting which led to REE enrichment in top and bottom soils [181]. In hypersaline groundwaters in Australia, 33–152 µg/L REE and enrichment of HREE due to higher complex stability of HREE-carbonate complexes compared to LREE were reported [108]. Colloidal particles may facilitate or retard REE migration along groundwater flow paths, which is highly dependent on the reversibility of the sorption process. Colloid particles in deep groundwaters mainly consist of quartz, clays, iron hydroxides, calcite, and humic substances [182]. At the Mizunami Underground Laboratory (Japan), it was found that up to 60% of the REE, particularly LREE, were associated with suspended particles, especially carbonates and Fe/Mn oxides [182]. Within the Dead Sea fault system (Israel), the northern spring is dominated by Ca-HCO₃. Further south, they contain sulfate from the dissolution of gypsum or high Na and Cl contents from ancient brines or meteoric waters dissolving halites. According to PHREEQC modeling, most well waters were undersaturated with gypsum and halites, but some were oversaturated with dolomite and calcite. The REE were either complexed by carbonate, chloride, or fluoride. The amount of REE³⁺ and [REECl]²⁺ species decreased with increasing molecular weight, whereas the amounts of [REE(CO₃)₂][−] increased, and [REECO₃]⁺ remained constant. The well waters grouped due to their low redox potential (−0.40 < Eh < −0.25) had a distinctly positive Eu anomaly but no Ce anomaly. In contrast, the other group (−0.1 < Eh < +0.26 V) had a strong Ce anomaly and was enriched in the middle REE [157].

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