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# Global Biogeochemical Cycles®



## REVIEW ARTICLE

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## The Global Biogeochemical Cycle of the Rare Earth Elements

### Special Collection:

The Elements Collection

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### Key Points:

- Rare earth elements (REE) are powerful tracers of both natural and anthropogenic processes within terrestrial and ocean environments
- REE are controlled by absorption, adsorption/desorption, co-precipitation, remineralization, and particle dissolution
- REE are technology-critical metals with broad applications in the future low-carbon global economy

### Supporting Information:

Supporting Information may be found in the online version of this article.

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**Abstract** To improve our understanding and guide future studies and applications, we review the biogeochemistry of the rare earth elements (REE). The REEs, which form a chemically uniform group due to their nearly identical physicochemical properties, include the lanthanide series elements plus scandium (Sc) and yttrium (Y). These elements, in conjunction with the neodymium isotopes, are powerful tools for understanding key oceanic, terrestrial, biological and even anthropogenic processes. Furthermore, their unique properties render them essential for various technological processes and products. Here, we delve into the characteristics of REE biogeochemistry and discuss normalization procedures and REE anomalies. We also examine the aqueous speciation of REEs, contributing to a better understanding of their behavior in aquatic settings, including the role of neodymium isotopes. We then focus on their environmental distribution, fractionation, and controlling processes in different environmental systems across the land-ocean continuum. In addition, we analyze sinks, sources, and the mobility of REEs, providing insights into their behavior in these environments. We further investigate the sources of anthropogenic REEs and their bioavailability, bioaccumulation, and transfer along food webs. We also explore the potential effects of climate change on the cycling, mobility and bioavailability of REEs, underlining the importance of current research in this evolving field. In summary, we provide a comprehensive review of REE behavior in the environment, from their properties and roles to their distribution and anthropogenic impacts, offering valuable insights and pinpointing key knowledge gaps.

## 1. Introduction

### 1.1. Definition, Classification, and Physicochemical Properties

Rare earth elements (REE) are a group of chemical elements that consist of the 15 lanthanides (La, lanthanum; Ce, cerium; Pr, praseodymium; Nd, neodymium; Pm, promethium; Sm, samarium; Eu, europium; Gd, gadolinium; Tb, terbium; Dy, dysprosium; Ho, holmium; Er, erbium; Tm, thulium; Yb, ytterbium; Lu, lutetium), as well as scandium (Sc) and yttrium (Y). Scandium and Y are included as REEs because they share similar properties and are found in the same column (III) of the periodic table. Notably, Pm is a lanthanide that is produced only through nuclear reactions and is virtually absent in nature.

REEs are commonly classified into two or three groups. According to the International Union for Pure and Applied Chemistry (IUPAC), the light rare earth elements (LREE) include La through Eu, whereas the heavy rare earth elements (HREE) consist of Gd through Lu. Another classification divides them based on their atomic weight into three groups: LREE (La to Pm), middle rare earth elements (MREE) (Sm to Gd), and HREE (Tb to Lu) (e.g., Johannesson & Lyons, 1995; Nakamura et al., 1997). Yttrium (Y) mimics the HREE, particularly Ho, because of the similarity in their ionic radii. On the other hand, Sc is a much smaller cation with a chemical behavior that differs from other REEs (Till et al., 2017) and is generally treated separately.

REEs exhibit unique properties such as magnetism, luminescence, electrochemical activity, and thermal characteristics. They are primarily found in the trivalent oxidation state in Earth surface systems (although other REE, for instance Ce can also occur in the tetravalent state, and Eu in the divalent state, as will be discussed later) and

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demonstrate similar physicochemical properties that systematically and gradually vary across the series. These similarities are the result of their electron configurations.

A progressive filling of the inner 4f electron shell throughout the series accompanies the gradual decrease in their ionic radii with increasing atomic number (i.e., the lanthanide contraction). This phenomenon happens due to the poor shielding effect of the 4f electrons. The poorer the shielding, the stronger the nuclear attraction to the electrons, causing decreased atomic radius with increased proton numbers, as observed in the lanthanide contraction. Another consequence of the lanthanide contraction is a general increase in ionization potential across the series. Therefore, REEs exhibit strong fractionation due to size and charge and significant “within-group” fractionation resulting from the lanthanide contraction.

The term “rare earth” can be misleading as some REEs (e.g., La and Ce) have a crustal abundance comparable to copper (Cu) and lead (Pb), and are more abundant than mercury (Hg) and platinum (Pt) (Lide & Haynes, 2009). Even the scarcest REEs (Lu and Tm) are more abundant in the Earth's crust than elements such as cadmium (Cd) and selenium (Se). However, REEs are widely dispersed in the Earth's crust, occurring in multiple mineral sources but with limited occurrences in economically viable ore deposits. Indeed, the similarity in the ionic radius and oxidation state among the REEs allows for their substitution within various crystal lattices. The slight differences in ionic radius across the series commonly result in the segregation of REEs into deposits enriched in either LREE or HREE, the latter including yttrium (Castor & Hedrick, 2006).

The growing interest in the REE cycle can be attributed to substantial advancements in analytical instrumentation, with inductively coupled plasma mass spectrometry (ICP-MS) playing a prominent role. This highly sensitive technique has revolutionized the field by enabling the accurate quantification of all REEs, even at extremely low concentrations ranging from nanomolar to picomolar levels, in complex environmental matrices such as seawater and groundwater. These analytical advancements have provided the means for laboratories around the world to conduct high-quality measurements of REEs in a wide variety of samples, including ocean, surface and groundwaters, rocks, and biological tissues, which has led to important discoveries of the biogeochemical processes that control REE concentrations and fractionation in the environment.

## 1.2. Roles—Micronutrients, Contaminants, Tracers, and Proxies

Since the last decades of the twentieth century, the REE's unique properties have made them essential tools for understanding key oceanic, terrestrial, and biological processes. Like other trace elements, such as Cu and zinc (Zn) (e.g., Anderson, 2020; Anderson et al., 2014), REEs may play multiple roles.

REEs were once believed to lack biological activity in organisms. However, despite their diminishing concentrations, in some cases REEs are preferably used over other more abundant elements. For example, despite the billion-fold greater concentrations of calcium (Ca) in natural environments compared to REEs, due to their similar ionic radius, they can likely displace Ca at Ca-binding sites in biological systems (Thomas et al., 2014). At low concentrations, REEs may act as micronutrients, enhancing crop yield (e.g., wheat, rice, maize) and livestock production (Pang et al., 2002; Tariq et al., 2020; Tommasi et al., 2021, 2023; M. Q. Wang & Xu, 2003). The concentration-dependent positive effects of REEs are grounded in hormesis, where mild environmental stressors, such as low doses of REE-based substances, yield beneficial outcomes. These applications have seen extensive use in China for more than three decades and have also been adopted in other countries including Japan, Australia, Switzerland, and Korea (Abdelnour et al., 2019; Turra, 2018; Tyler, 2004; M. Q. Wang & Xu, 2003).

Over the last 10 years, studies have revealed the evolving roles of REEs in organic carbon metabolism (Keltjens et al., 2014; Nakagawa et al., 2012; Picone & den Camp, 2019; Reitz & Medema, 2022; Shiller et al., 2017). Analysis of a global ocean metagenomic/metatranscriptomic data set indicates the widespread presence of lanthanide (Ln)-dependent methanol-, ethanol-, sorbose-, and glucose-dehydrogenases across all metagenomes, with numerous individual organisms hosting dozens of unique Ln-dependent genes (Voutsinos et al., 2023). This data set also suggests that biological methanol oxidation in the majority of surface ocean areas is predominantly Ln-dependent. Nonetheless, the mechanisms governing REE acquisition and transport as well as the global distribution and biogeochemical significance of lanthanide-dependent metabolism remain largely unknown (Shiller et al., 2017; Takahashi et al., 2007; Voutsinos et al., 2023).

Similar to other trace elements, REEs are influenced by anthropogenic activities. They are crucial components of high-tech products, including “smartphone” miniaturized speakers, contrast agents for magnetic resonance

imaging in medicine, and components of low-carbon energy and transportation systems such as electric vehicles, solar panels, and wind turbines (Balaram, 2019; Castor & Hedrick, 2006; Haxel, 2002). Consequently, the fast-growing demand for REE has led to an increase in global mining and REE inputs that can disrupt natural biogeochemical cycles and cause REE contamination in water, sediments, and biota (R. L. Andrade et al., 2020; Bau & Dulski, 1996a; Delgado et al., 2012; Hatje et al., 2016; Merschel & Bau, 2015; Pedreira et al., 2018; Pinto et al., 2019). Therefore, depending on their concentration, REE can act as both micronutrients and contaminants, exhibiting various toxic effects, as will be discussed further.

Due to their chemically coherent behavior, REEs provide valuable insights into petrogenic, geochemical, and oceanic processes that other single or multiple element tracers cannot distinguish. In addition, the isotopic composition (IC) of Nd is used as a tool in reconstructing ocean circulation in the modern as in the past ocean (Abbott, Haley, McManus et al., 2015; Hathorne et al., 2015; Jeandel, 1993; Lacan & Jeandel, 2005; Piepgras & Wasserburg, 1982, 1987; van de Flierdt et al., 2016). Nd composition is typically expressed in the epsilon notation:

$$\epsilon\text{Nd} = \left[ \left( \frac{{}^{143}\text{Nd}_{\text{sample}}/{}^{144}\text{Nd}_{\text{sample}}}{{}^{143}\text{Nd}_{\text{CHUR}}/{}^{144}\text{Nd}_{\text{CHUR}}} \right) - 1 \right] \times 10^4 \quad (1)$$

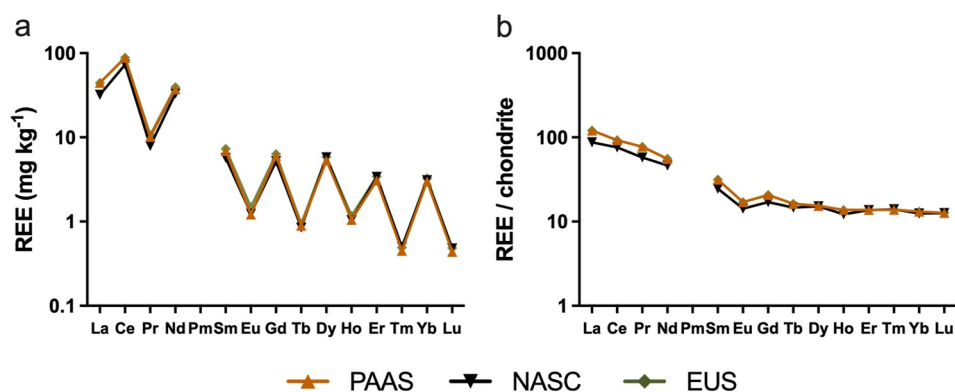
where CHUR is the chondritic uniform reservoir used as an average Earth value ( ${}^{143}\text{Nd}/{}^{144}\text{Nd} = 0.512638$ ) (Jacobsen & Wasserburg, 1980).

The most important scientific step forward obtained by coupling the analysis of Nd isotopes to that of the REE (and mostly Nd) concentrations in the ocean was to reveal what was called the “Nd paradox.” The “Nd paradox” is the term used to name the partial decoupling between Nd concentrations and isotopic compositions in the ocean (Goldstein & Hemming, 2003; Jeandel et al., 1995, 1998; Johannesson & Burdige, 2007; Tachikawa et al., 2003; van der Flierdt et al., 2004). The isotopic constraint revealed that the Nd oceanic budget was not balanced and that an important “missing source” was required to balance both the Nd isotopic signature and concentration along the Atlantic-Pacific conveyor belt (Goldstein & Hemming, 2003; Tachikawa et al., 2003). This missing source, required to modify the isotopic signatures while the concentration was barely changing, was called “Boundary Exchange” (or BE) by Lacan and Jeandel (2005) since these authors strongly suggested that the main mechanism explaining the paradox was occurring along the oceanic margins. However, these authors could not identify the mechanisms leading to this “exchange,” which will be discussed in the next sections.

The REE abundance pattern, along with the redox-sensitive element Ce, and Nd isotopic composition, can be used for reconstructing past environmental conditions and studying weathering, sediment provenance, and climate change that occurred on the continents in the past (Frank, 2002; X. Liu et al., 2019; Sousa et al., 2022; Taylor & McLennan, 1985; Tachikawa et al., 2017). REE serve as powerful geochemical tracers for the characterization of igneous rock formation conditions, water mass origin and fate while transported by ocean currents, and determination of sediment sources, in addition to helping characterize scavenging processes, particle-solution exchange, present and past oceanic circulation patterns, and changes in submarine groundwater discharge and mixing (Alibo & Nozaki, 2004; Bigot et al., 1984; Elderfield, 1988; Haley et al., 2014; Johannesson et al., 2011; Johannesson, Stetzenbach, & Hodge, 1997; Jeandel, 1993; Piepgras & Wasserburg, 1982, 1987; X. Y. Zheng et al., 2016). Furthermore, they are effective tracers for identifying anthropogenic REE inputs and dispersion in the environment, helping to identify contamination from mining, industrial activities, agriculture, as well as hospital and domestic wastewater (Bau & Dulski, 1996a; Hatje et al., 2014; Kulaksiz & Bau, 2013; Mirlean et al., 2020; Romero et al., 2010, among many others). In addition, because of the similar valence and ionic radii of the REE and trivalent actinides (e.g.,  $\text{Am}^{3+}$ -americium,  $\text{Cm}^{3+}$ -curium, and  $\text{Cf}^{3+}$ -californium), the REEs are analogs for these radioactive transuranics and may be used to safely study their behavior in the environment (Choppin, 1983; R. Silva & Nitsche, 1995).

### 1.3. Presentation and Normalization Procedures

The Oddo-Harkins rule states that elements with even atomic numbers are more abundant in the solar system compared to those with odd atomic numbers. As a result, when plotting the abundance of REEs against their



**Figure 1.** Abundances of Rare Earth Elements (REE) in various shales used for normalization. (a) logarithmic plot of abundances of REE in Post-Archean Australian Shale (PAAS; Pourmand et al., 2012), North American Shale Composite (NASC; McLennan, 1989), and European Shale (EUS; Bau et al., 2018) and (b) the same data after normalization to chondrite (Taylor & McLennan, 1985).

atomic number or ionic radius, a zig-zag pattern emerges (Figure 1a), making data interpretation complex. To address this issue, REE concentration data are normalized against a natural reference standard, such as water or rock (e.g., Masuda, 1962). This smooths out the natural Oddo-Harkins distribution of REEs (Figure 1b), simplifying data interpretation and enabling comparisons among different environmental matrices. Normalization also facilitates the identification and quantification of REE anomalies, which are deviations from the smooth normalized pattern. Anomalies may indicate either REE enrichment or depletion. By having a normalized baseline, expected REE concentrations can be interpolated or extrapolated from the smooth REE pattern, making it easier to detect and analyze anomalous behavior (e.g., Bau et al., 2018; Rétif et al., 2023). Furthermore, the smoothness of the normalized pattern allows for a qualitative assessment of the analytical quality of the data (Bau et al., 2018).

There is a multitude of normalizing agents in the literature (Table 1). The selection of the most suitable normalizing agent depends on several factors including the research objectives, the specific matrix being studied, the geographical location, and the specific aspects that need to be emphasized. In addition, the normalizing agent should represent the source of the REE in the sample, enabling the examination of fractionation across the lanthanide series compared to the REE pattern in the source. Detailed criteria whereby reference standards are (or should be) chosen have recently been reviewed (Rétif et al., 2023).

Among the various options, two materials are commonly employed for REE normalization: shales and chondrites. Shales represent the average composition of the upper continental crust and are used in studies related to environmental geochemistry and ocean research. On the other hand, chondrites are representative of the bulk composition of the Earth and find application in studies focused on igneous geochemistry and cosmochemistry. The choice between shales and chondrites depends on the specific field of study and the research context.

In surface Earth sciences, the most widely used normalizing agent is the Post-Archean Australian Shale (PAAS), proposed in 1976 (Nance & Taylor, 1976) and refined in 1989 (McLennan, 1989). A more recent study conducted in Australia utilized a distinct set of shale samples and directly measured all REEs, unlike earlier studies that had estimated the concentrations of Tm and Lu. The findings of this study align closely with previous research, with slightly elevated concentrations of LREE due to improved accuracy in REE measurements and the resulting smoother normalized REE patterns (Pourmand et al., 2012). PAAS has been used for several matrices, including sediments, soils, fresh and marine waters, and biological samples.

Another shale standard commonly utilized for normalization is the North American Shale Composite (NASC) (M. A. Haskin & Haskin, 1966). NASC consists of a compilation of 40 samples, with 20 sourced from the United States and the remaining 20 collected from Zimbabwe, Antarctica, and unknown locations.

The European Shale (EUS) originally described in 1935 (Minami, 1935) and revised in 1966 (L. A. Haskin et al., 1966; M. A. Haskin & Haskin, 1966) has recently been improved and although it was recommended for normalizing shale samples originating from Europe (Bau et al., 2018), it is preferable to use a more widely applied

**Table 1**  
*REE and Y Concentrations (mg kg<sup>-1</sup>) in Different Shale Reference Materials Used for REE Normalization*

	PAAS <sup>a</sup>	PAAS <sup>b</sup>	PAAS <sup>c</sup>	NASC <sup>d,e</sup>	NASC <sup>b</sup>	UCC <sup>f</sup>	UCC <sup>g</sup>	EUS <sup>e</sup>	EUS <sup>h</sup>	MUQ <sup>i</sup>	WRAS <sup>j</sup>	WRAC <sup>j</sup>
Y	28	27	27.31	27	27	20.7	21	31.8	31.9	31.85	29.40	29.84
La	38	38.2	44.56	32	32	32.3	31	41.1	44.3	32.51	37.80	44.61
Ce	80	79.6	88.25	70	73	65.7	63	81.3	88.5	71.09	77.7	89.2
Pr	8.9	8.83	10.15	7.9	7.9	6.3	7.1	10.4	10.6	8.46	8.77	9.69
Nd	32	33.9	37.32	31	33	25.9	27	40.1	39.5	32.91	32.69	35.6
Sm	5.6	5.55	6.884	5.7	5.7	4.7	4.7	7.30	7.30	6.88	6.15	6.70
Eu	1.1	1.08	1.215	1.24	1.24	0.95	1	1.52	1.48	1.57	1.188	1.383
Gd	4.2	4.66	6.043	5.21	5.2	2.8	4	6.03	6.34	6.36	5.19	5.37
Tb	0.77	0.774	0.8914	0.85	0.85	0.5	0.7	1.05	0.944	0.99	0.819	0.831
Dy	4.4	4.68	5.325	5	5.8	2.9	3.9	-	5.86	5.89	4.95	4.87
Ho	1	0.991	1.053	1.04	1.04	0.62	0.83	1.20	1.17	1.22	1.019	0.980
Er	2.9	2.85	3.075	3.4	3.4	-	2.3	3.35	3.43	3.37	2.97	2.78
Tm	0.5	0.405	0.451	0.5	0.5	-	0.3	0.56	0.492	0.51	-	-
Yb	2.8	2.82	3.012	3.1	3.1	1.5	2	3.29	3.26	3.25	3.01	2.72
Lu	0.5	0.433	0.4386	0.48	0.48	0.27	0.31	0.58	0.485	0.49	0.456	0.406

*Note.* PAAS, Post-Archean Australian Shale; NASC, North American Shale Composite; UCC, Upper Continental Crust; EUS, European Shale; MUQ, Mud from Queensland; WRAS, World River Average Silts and WRAC, World River Average Clays. <sup>a</sup>Nance & Taylor (1976), <sup>b</sup>McLennan (1989), <sup>c</sup>Pourmand et al. (2012), <sup>d</sup>L. A. Haskin et al. (1966), <sup>e</sup>M. A. Haskin & Haskin (1966), <sup>f</sup>Wedepohl (1995), <sup>g</sup>Rudnick & Gao (2003), <sup>h</sup>Bau et al. (2018), <sup>i</sup>Kamber et al. (2005), <sup>j</sup>Bayon et al. (2015).

standard, such as PAAS, to ensure that all REE data are comparable. Despite the different source materials, all these shale standards exhibit similar concentration values (Table 1) and remove the zig-zag pattern. Consequently, the REE normalized pattern derived from the use of PAAS, NASC, and EUS does not significantly impact their interpretation (Bau et al., 2018; Rétif et al., 2023).

Similar to shales, there are also several chondrite reference materials (Masuda, 1975; McDonough & Sun, 1995; Taylor & McLennan, 1985) and other standards less commonly employed for normalizing REEs. One example is the Mid-Ocean Ridge Basalt (MORB; Taylor & McLennan, 2002), which represents the composition of the upper mantle, differing from other representatives of the continental crust that might be of interest in marine geochemical research. Likewise, the World River Average Silts (WRAS) and World River Average Clay (WRAC; Bayon et al., 2015) serve as representative samples of the average composition of the weathered and eroded upper continental crust from rivers around the world. These references are suitable for investigating REEs in freshwater systems. For unconsolidated sediments there is the Mud from Queensland (MUQ), a composite of alluvial fine-grained sediment samples from Australia (Kamber et al., 2005). Another reference is the Upper Continental Crust (UCC), originally proposed in 1985 (Taylor & McLennan, 1985), revised in 1995 (Wedepohl, 1995) and further revised in 2003 (Rudnick & Gao, 2003). UCC represents sedimentary rocks and glacial deposits of the upper continental crust.

Shales and chondrites differ greatly from biological matrices regarding REE composition and nature, although both have been previously used to normalize biological samples (de Sena et al., 2022; Santos et al., 2023; Squadrone et al., 2017). Because of the differences among matrices, it is challenging to identify inter-sample deviations when using shales and chondrites for biological sample normalization. Consequently, it is recommended to employ matrix-matched samples (i.e., organisms from the same order) for normalization, enabling the identification of fractionation, geogenic anomalies, and anthropogenic influences on REE concentrations in biological samples (Rétif et al., 2023). However, so far no reference material specific to biological samples has been proposed.

In many cases, it is preferable to normalize REE concentrations using a local and/or a matrix-matched normalizing agent. This local or matrix-matched reference sample may present inter-element concentrations

much closer to those of the study sites than the shales and chondrite references usually employed. Local normalization permits the assessment of subtle variations between samples that might otherwise go unnoticed. Besides, this normalization is essential to distinguish contributions to the total REE concentration derived from natural processes (i.e., background REE concentrations) from anthropogenic ones (Bau et al., 2018). This approach has been used, for instance, in marine studies, where local seawater is used in combination with PAAS normalization to enhance data interpretation (Haley & Klinkhammer, 2003; Hatje et al., 2016; Nozaki et al., 1999).

#### 1.4. REE Anomalies From Redox Chemistry and Complexation

REEs generally exist in nature in the +III oxidation state and they form  $M^{3+}$  cations in aqueous solution. Under conditions that occur in and on the Earth's crust, only cerium can be oxidized to Ce(IV) and europium reduced to Eu(II), which are, respectively, more and less particle-reactive than their trivalent REE neighbors. The different geochemical behavior that results from such transformations leads to inter-element fractionation that can be observed as anomalies in the normalized REE pattern.

The quantification of anomalies required to compare different samples and studies remains one of the most debated and confounding topics in REE geochemistry. Rétif et al. (2023) extracted 15–20 different equations from the literature for each of the anomalies of Ce, Eu, and Gd. Although simple inter-element ratios can be used (e.g., Ce/Nd), more commonly the abundance of an anomalous element is compared to what it is expected to be from the behavior of its neighbors in the REE pattern. The latter is written as  $Ln_x^*$ , where  $Ln_x$  indicates an REE (lanthanide) with atomic number  $x$  and the anomaly is calculated as  $[Ln_x]/[Ln_x^*]$ , with all abundances normalized to a suitable standard. The value of  $[Ln_x^*]$  can be calculated as a simple interpolation between its immediate neighbors on either side (Alibo & Nozaki, 1999):

$$[Ln_x^*] = \frac{([Ln_{x-1}] + [Ln_{x+1}])}{2} \quad (2a)$$

or for more distant neighbors:

$$[Ln_x^*] = \frac{(j \times [Ln_{x-i}] + i \times [Ln_{x+j}])}{(i + j)} \quad (2b)$$

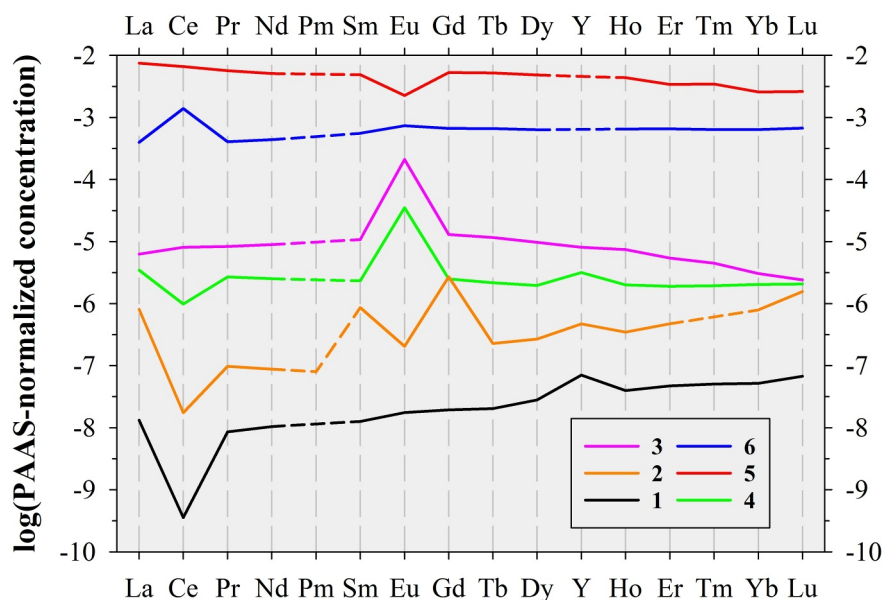
with  $i, j > 0$ , which is also valid for extrapolations, that is, if both neighbors are on the same side of  $Ln_x$  ( $i < 0$  or  $j < 0$ ). If the REE pattern is exactly linear, that is, of the form  $[Ln_x^*] = ax + b$ , the two equations are equivalent. However, if the pattern is curved, Equation 2b will increasingly underestimate or overestimate the anomaly for larger values of  $i$  and  $j$  depending on whether the curvature is convex or concave. In that case, it is more appropriate to use a geometric mean (Lawrence & Kamber, 2006):

$$[Ln_x^*] = [Ln_{x-i}]^{j/(i+j)} \times [Ln_{x+j}]^{i/(i+j)} \quad (3a)$$

or, equivalently:

$$\log[Ln_x^*] = \frac{(j \times \log[Ln_{x-i}] + i \times \log[Ln_{x+j}])}{(i + j)} \quad (3b)$$

The REE patterns are commonly displayed on a log scale, which tends to linearize them and provoke the use of Equation 2b, even when Equation 3b is the better choice (note their similarity, except for the log conversion). This is exacerbated by the fact that the ratio  $[Ln_x]/[Ln_x^*]$  is typically expressed on a log scale to more easily distinguish enrichment ( $[Ln_x]/[Ln_x^*] > 1$ , hence  $\log([Ln_x]/[Ln_x^*]) > 0$ ) from depletion ( $[Ln_x]/[Ln_x^*] < 1$  thus  $\log([Ln_x]/[Ln_x^*]) < 0$ ), which is why these are referred to as positive and negative anomalies, respectively (e.g., Elderfield & Greaves, 1981). A recent review and rigorous mathematical treatment recommends that Equation 3a should always be used as it is more robust and makes the anomaly calculation less dependent on the type of normalization (Barrat et al., 2023). With any of the equations above, the uncertainty of the anomaly can be estimated by suitable mathematical propagation of analytical errors for the REE concentrations (Beers, 1957). It may be noted that,



**Figure 2.** Examples of Rare Earth Elements (REE) patterns with distinctive single-element anomalies. Anomalies of Y are emphasized by placing it between Dy and Ho; the three elements have similar ionic radii, but Y has more ionic properties due to its lack of *f*-electrons. Non-reported elements were interpolated between immediate neighbors, except Pm in pattern 2, which was extrapolated from Pr and Nd to emphasize the Sm anomaly. All patterns were normalized to the revised PAAS values of Pourmand et al. (2012). Patterns 1, 5, and 6 were vertically shifted by  $-1$ ,  $-4$  and  $-3$  log units, respectively, for clarity. (1) South-Pacific seawater (station SO225-21-1, 3,992 m) with characteristic negative Ce and positive Y anomalies (Molina-Kescher et al., 2018). (2) River Rhine at Leverkusen (Germany) during low-flow conditions (7 Nov 2011). Positive anomalies are due to contaminants from medical facilities (Gd) and a cracking catalyst plant (La and Sm) upstream (Kulaksiz & Bau, 2013). (3) Hydrothermal fluid (sample BS-13-4/2) from the Mid-Atlantic Ridge with a strong positive Eu anomaly (Bau & Dulski, 1999). (4) Discharge from the SWS diffuse vent site on the Juan de Fuca Ridge. The presence of both a negative Ce and positive Eu anomaly indicates extensive mixing of the hydrothermal fluid with ambient seawater (Bao et al., 2008). (5) Fluid inclusion in granophyre (sample CPU-2). The negative Eu anomaly is a host signature of the granitic magma with which it was at equilibrium (Banks et al., 1994). (6) Manganese nodule (sample D535) from the South Pacific Ocean with a positive Ce anomaly due to oxidation on the  $\delta$ -MnO<sub>2</sub> surface (Takahashi et al., 2000).

whereas the majority of natural Ce anomalies are negative, common laboratory contaminants like dust tend to have a shale-like REE pattern. Usually, blanks and hence analytical errors are thus proportionally larger for Ce than for the other LREEs.

More subtle REE anomalies (e.g., for Y, La, Gd) may be due to the tetrad effect (Kawabe et al., 1998; McLennan, 1994; Takahashi, Yoshida, et al., 2002) which, for example, makes Y less covalently bound in complexes and thus less particle-reactive than Ho (Bau, 1999; Nozaki et al., 1997) (Figure 2, pattern 1). This phenomenon is caused by spin-pairing effects in REE binding to different anions (Kawabe, 1992) and is most prominent when REEs are fractionated in precipitation-dissolution systems (Takahashi, Yoshida, et al., 2002). It is less pronounced for REE sorption, where the similar REE fractionations of opposing surfaces and solution complexation are canceled out (Tao et al., 2004).

Some anomalies (Figure 2, pattern 2) indicate the input of a single REE as contaminants (Kulaksiz & Bau, 2013; Rogowska et al., 2018). Different approaches have been proposed to quantify these and other REE fractionation effects, including multi-element ratios (Monecke et al., 2002; Osborne et al., 2015) and polynomial fits (Möller et al., 2002).

The reduction of Eu(III) in aqueous solutions only proceeds readily at temperatures above  $\sim 250^{\circ}\text{C}$  and high pressure (Sverjensky, 1984). Such conditions are uncommon in natural waters and mostly occur in underground hydrothermal systems. As Eu<sup>3+</sup> is reduced to the much larger Eu<sup>2+</sup> cation, it becomes less compatible with its crystal lattice sites in the host rock and is preferentially leached into the hydrothermal fluid, leading to a strong relative Eu enrichment, that is, a positive anomaly (Klinkhammer et al., 1994). Very large ( $>10$ ) positive Eu anomalies have been found in hot fluids emanating from vents along submarine spreading ridges (Bao et al., 2008;

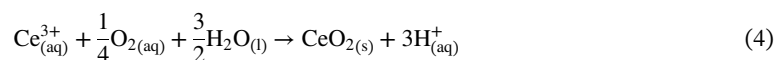


Hongo et al., 2007; Klinkhammer et al., 1994; Michard, 1989; Olivarez & Owen, 1991), as exemplified by pattern 3 in Figure 2. As the fluid is rapidly diluted by cold, oxygenated seawater, Eu is re-oxidized and scavenged by ferromanganese oxides that copiously precipitate within the buoyant plume (Klinkhammer et al., 1983; Olivarez & Owen, 1989). As mixing and scavenging progress, the solution rapidly loses the hydrothermal REE signature and acquires the characteristic REE signature of seawater (Figure 2, pattern 1), whereby intermediate patterns with both a negative Ce and positive Y and Eu anomalies have been observed in both the solution (Figure 2, pattern 4) and plume particles (German & Elderfield, 1990; Grenier et al., 2013; Klinkhammer et al., 1994).

Positive Eu anomalies in natural waters do not always reflect in situ reduction as they can be inherited as a source signature of rocks with which the solution is at equilibrium. The larger  $\text{Eu}^{2+}$  cation more readily partitions into minerals such as plagioclase and orthoclase feldspar, a major component of, for example, North-African dust (Pourmand et al., 2014). Similarly, negative Eu anomalies in solution, which are not readily explained in terms of in situ redox processes, can be inherited from previously Eu-depleted minerals or melts (Figure 2, pattern 5).

Unfortunately, polyatomic interferences during ICP-MS analyses of environmental samples can lead to spurious (typically positive) Eu anomalies (Jiang et al., 2007) that are relatively widespread in the literature and often unrecognized, leading to erroneous conclusions. Indeed, both isotopes,  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$ , overlap with oxide ions of Ba ( $\text{Ba}^{16}\text{O}^+$ ) that form in the argon plasma (Dulski, 1994; Smirnova et al., 2006). Whereas it is commonly argued that Ba can be removed by preparatory chromatography, many natural samples have Ba/Eu ratios over 1000, so removing >99% may still leave analyte and interferent signals of comparable size. Any residual interference is moreover challenging to discern because the ratio of the interfering Ba isotopes ( $^{135}\text{Ba}/^{137}\text{Ba} \sim 0.59$ ) is similar in magnitude to that of the Eu isotopes ( $^{151}\text{Eu}/^{153}\text{Eu} \sim 0.92$ ), that is, even if the total BaO and Eu signals are of equal size, the Eu isotope ratio will change by no more than a few percent, whereas the apparent Eu concentration would double. Although the introduction of new techniques such as in-line sample preparation and desolvating nebulization systems have greatly improved the suppression of interferences in ICP-MS analyses of environmental REE samples (Wysocza, 2021), these innovations are not yet routinely implemented.

The oxidation of Ce(III) to Ce(IV) is commonly taken to proceed in the presence of free oxygen, for example, as follows:



with a half-reaction potential falling between the equivalent oxidations of  $\text{Mn}^{2+}$  to  $\text{Mn(IV)O}_2$  and  $\text{Fe}^{2+}$  to  $\text{Fe(III)(OH)}_3$ . Whether the product is assumed to be  $\text{CeO}_2$  or  $\text{Ce(OH)}_4$ , it is clear that the oxidation is strongly pH-dependent and suppressed at low pH. At elevated pH, the oxidation is more likely to involve hydrolyzed Ce(III) species such as  $\text{CeOH}^{2+}$  (Yu et al., 2006). A speciation model (de Baar et al., 1988) showed that the seawater concentration of total dissolved Ce in equilibrium with  $\text{CeO}_2(\text{s})$  should be exceedingly low ( $<10^{-15}$  M). It is therefore more likely that Ce oxidation occurs at the surface of particles upon sorption of  $\text{Ce}^{3+}$  (Figure 2, pattern 6). The resulting  $\text{Ce}^{4+}$  ion is much more strongly bound, causing enhanced retention of Ce relative to the trivalent REE and a negative Ce anomaly in the solution (Figure 2, pattern 1). In suboxic to anoxic waters, Ce(IV) is reduced and released from particles, causing the Ce anomaly to disappear or sometimes become modestly positive (de Baar et al., 1988; German et al., 1991; German & Elderfield, 1989; Schijf et al., 1994, 1995; Tachikawa, Jeandel, & Roy-Barman, 1999; Tachikawa, Jeandel, Vangriesheim, & Dupré, 1999).

The ostensibly direct relationship between the presence of free oxygen and the Ce anomaly gave rise to the idea that the latter might be used as a proxy of the redox status of the paleo-ocean, provided that the seawater Ce anomaly signal is transferred to and permanently preserved in the marine sedimentary record (Hodel et al., 2021). The seawater signal is believed to be most reliably recorded by authigenic phases such as carbonates, phosphates, ferromanganese oxides, and chert. Sedimentary phosphates display a bewildering range of REE patterns that largely appear to be post-depositional (Bright et al., 2009; Reynard et al., 1999; Shields & Stille, 2001) and suitable samples must be selected with the utmost care (Jiang et al., 2007; Morad & Felitsyn, 2001). Studies on carbonates and chert are more promising (Ding et al., 2022; Q. Guo et al., 2007; MacLeod & Irving, 1996; Tostevin et al., 2016) as their REE patterns may be less prone to alteration (X. Liu et al., 2019). A notable advance has been recognizing the need for careful sample preparation to avoid interference from REE-rich contaminant

phases (Cao et al., 2020). Unfortunately, whereas it was found early on that foraminiferal REE signals are primarily contained in external ferromanganese oxide coatings (Palmer & Elderfield, 1986), it appears that these are commonly microscopically intercalated with the sample to a level where they cannot be effectively removed (Tachikawa et al., 2013).

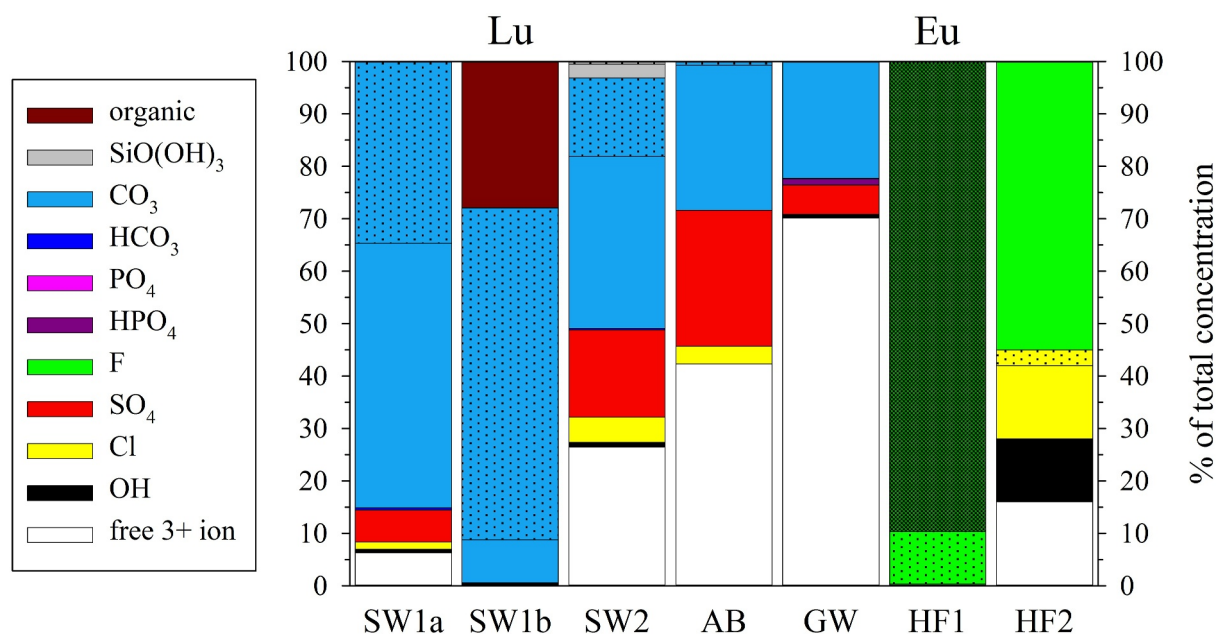
Despite ongoing progress, the interpretation of sedimentary Ce anomalies remains a source of controversy and confusion due to uncertainty about what signal is actually recorded and where (Osborne et al., 2017; Skinner et al., 2019). Whereas a particle at equilibrium may acquire a seawater REE pattern directly, the negative Ce anomaly of seawater presumably arises because Ce is more efficiently scavenged than the trivalent REE. One might therefore argue that oxidizing conditions should leave bulk particulates with a positive Ce anomaly (Tachikawa, Jeandel, & Roy-Barman, 1999; Wilde et al., 1996). Besides redox conditions, the Ce anomaly may be sensitive to other influences, such as water depth and depositional setting (Murray et al., 1991) or freshwater inputs (Johannesson et al., 2006; Y. Zhao et al., 2021). Whereas it is known that Ce oxidation can be catalyzed on the surface of Mn oxides (Lagarde et al., 2020; Moffett, 1990; Takahashi et al., 2007; Tanaka et al., 2010), there is also a growing realization that it can be promoted by a variety of inorganic (Riglet-Martial et al., 1998; Yu et al., 2006) and especially organic ligands (Cervini-Silva et al., 2008; Deng et al., 2020; Seto & Akagi, 2008; Yoshida et al., 2004), even under anoxic conditions (Kraemer & Bau, 2022). This level of complexity is not yet adequately captured by either thermodynamic (Cao et al., 2022) or steady-state (Bellefroid et al., 2018) oxidation models. On the other hand, analytical developments, such as the ability of synchrotron X-rays to probe the Ce oxidation state in situ (Takahashi, Sakami, & Nomura, 2002), have sparked a recent resurgence of the field. Initially, gloomy assessments of its potential (Holser, 1997; Pattan et al., 2005) are lately sounding a more hopeful note (Skinner et al., 2019; K. Zhang & Shields, 2022). Along its predictable trajectory in the Elderfield Paleoceanographic Proxy Confidence Factor Phase Chart (PPCPP) (Elderfield, 2002), the Ce paleo redox proxy may finally be moving from the “pessimism phase” into the “realism phase.”

### 1.5. Aqueous Speciation of Yttrium and the REE

The term aqueous speciation refers to the distribution of a metal among its dissolved species including complexes with all available organic and inorganic ligands. A key variable is the relative contribution of the free hydrated or uncomplexed cation, expressed as a fraction of the total metal concentration, which controls solubility, reactivity toward particles, and possibly uptake by organisms (Weltje et al., 2004). Interactions with individual ligands are also important, as some complexes have been found to intensify metal sorption on certain particle surfaces (Davranche et al., 2004), whereas specific organic ligands may promote bioavailability and thereby facilitate microbial acquisition of essential metals (Butler, 1998).

Speciation modeling involves solving a system of equations comprising mass balances for all relevant metals and ligands as well as mass action expressions for the pertinent complexation reactions (F. Morel & Morgan, 1972). The latter requires thermodynamic equilibrium constants for each reaction at conditions appropriate to the solution at hand. These so-called stability constants are functions of temperature, pressure, and solution composition, that is, ionic strength. The relative contribution of a complex to the speciation depends only on the stability constant and the free-ligand concentration, but not on the concentration of the metal, provided it is much smaller than that of the ligand (Bruno, 1997; Christenson & Schijf, 2011; Millero, 1992). It follows that this contribution may be significant either when the complex is very stable, the ligand very abundant, or both.

The complexation of yttrium and the REEs with numerous organic and inorganic ligands has been studied over a wide range of conditions. The evolving database of stability constants has been reviewed or critically evaluated multiple times (Byrne & Sholkovitz, 1996; Millero, 1992; Schijf & Byrne, 2021; Wood, 1990a). REEs are classified as hard acid cations with a particular affinity for ligands that contain oxygen functional groups (Turner et al., 1981). However, unlike metals that are extensively hydrolyzed, such as Be and Th, or that greatly favor a single ligand, such as chloride for Ag and Cd (Byrne, 2002), the REEs form a variety of species. The most stable inorganic ones are the first- and second-order complexes with, respectively, one and two carbonate anions. The current consensus has REE speciation dominated by these carbonate complexes in most alkaline waters, notably in seawater. Nevertheless, the REEs also form stable complexes with phosphate, silicate, and fluoride, which may prevail in situations where carbonate complexation is suppressed. Even the comparatively weak REE ligands sulfate and chloride may be prominent in waters of unusual composition. Whereas the REEs have a substantial tendency to hydrolyze, hydrolysis is typically minor in the presence of stronger ligands. Turner et al. (1981) have



**Figure 3.** Modeled speciation of lanthanum (La), except as labeled above the columns, in various natural waters. Species contributions are shown as fractions of the total rare earth elements (REE) concentration. Bars in each column are stacked as shown in the legend. Contributions less than 0.5% cannot be resolved in the graph. Second-order (e.g.,  $\text{EuF}^{+}_2$ ) and third-order (e.g.,  $\text{EuF}^0_3$ ) complexes are indicated with light and heavy stippling, respectively. SW1a is standard surface seawater ( $S = 35$ ) at  $T = 25^\circ\text{C}$ . Speciation of the heaviest REE (Lu) is shown for comparison (SW1b). Organic complexation is modeled as a single strong ligand (trihydroxamate siderophore desferrioxamine B) at a fixed free concentration of  $10^{-13}$  M (Christenson & Schijf, 2011). SW2 is adjusted for deep ocean conditions ( $T = 2^\circ\text{C}$ ,  $P = 500$  atm) (Schijf & Byrne, 2021). AB is the anoxic, hypersaline lower brine of the Bannock Basin in the eastern Mediterranean (Schijf et al., 1995). GW is the model groundwater of Wood (1990a), recalculated with new stability constants by Johannesson, Stetzenbach, et al. (1996), at pH 7. HF1 is the model hydrothermal fluid of Wood (1990b) at  $T = 100^\circ\text{C}$  and  $P_{\text{sat}}$  with a total fluoride concentration of  $10^{-4}$  m; Eu speciation is shown (his Figure 18b). HF2 is the model hydrothermal fluid of Haas et al. (1995) at  $T = 300^\circ\text{C}$  and  $P_{\text{sat}}$  (their Fig. 8). The composition of HF2 is similar to that of HF1, except for tenfold higher concentrations of fluoride and sulfate; both are shown at pH 5.

argued that their affinity for both carbonate and hydroxide also gives the REE a propensity for organic complexation. The marine geochemistry of metals with this preference, such as Fe and Cu, can be completely governed by organic complexes. Although some biogenic and anthropogenic REE ligands have been identified (Christenson & Schijf, 2011; Cotruvo Jr. et al., 2018; Schijf & Byrne, 2001), the extent of organic REE complexation in natural waters remains unknown to some degree.

The next paragraphs provide a summary of our present understanding of REE speciation in seawater and other alkaline waters, in waters where carbonate is not the primary ligand, and in hydrothermal fluids. Examples are shown in Figure 3 for surface and deep seawater, a brine, a model groundwater, and two model hydrothermal fluids, focusing on the lightest element, La. For seawater, the speciation of Lu, the heaviest element, is added for comparison to illustrate the full range of REE behaviors. Critical knowledge gaps are emphasized, for instance, ligands that have been inadequately studied and the influence of pressure at low temperatures.

Seawater is by far the most common natural solution, yet it is rather unique because of its high ionic strength ( $I \sim 0.7$  M) and almost constant composition throughout the ocean at all depths; its elevated pH ( $\sim 8$ ), which increases the fraction of free carbonate; and its high concentrations of the weaker ligands, chloride and sulfate. Marine REE speciation was recently summarized by Schijf and Byrne (2021) and is shown in Figure 3 (columns SW1a, b) for the ocean surface. It is dominated by carbonate for all REEs, ranging from  $\sim 85\%$  to  $99\%$  of total concentrations, in the absence of organic complexes. From La to Lu, the fraction of second-order complex increases to gradually match and then exceed that of the first-order complex. Contributions of the free cation and the sulfate complex (each  $\sim 6\%$ ) and of the chloride and hydroxide complexes ( $0.5\%–1.5\%$ ) are significant for La yet decline across the series to negligible levels. The dominance of carbonate, especially the contribution of higher-order complexes, can be even greater in solutions more alkaline than seawater. Möller and Bau (1993) observed REE patterns with an unusual positive Ce anomaly in the waters of Turkish Lake Van (pH  $\sim 9.6$ ), which they attributed to the intriguing possibility of dissolved Ce(IV) being stabilized as a highly anionic fifth-order carbonate complex. Smaller positive

Ce anomalies have been observed in Mono Lake, California (pH  $\sim$  9.8), where the second-order carbonate complex comprises >99% of each dissolved REE (Johannesson & Lyons, 1994). Conversely, REE carbonate complexation may be strongly suppressed in the hypersaline submarine brine of Bannock Basin (Schijf et al., 1995), leading to free-cation fractions of up to >40%, as shown in Figure 3 (column AB). In addition to lower pH ( $\sim$ 7.6), this is caused by competition for the carbonate ligand by excess  $Mg^{2+}$  and  $Ca^{2+}$ .

The importance of organic REE complexation is uncertain, although their chemical properties suggest that it may be considerable (Turner et al., 1981). Metals whose marine geochemistry is controlled by organic complexes seem to have an overwhelming affinity for a small number of extremely strong and highly specific ligands (Vraspir & Butler, 2009). That may also apply to the REE as well is indicated by recent evidence that some are a ubiquitous component of key microbial enzymes (Cotruvo Jr. et al., 2018; Shiller et al., 2017). Christenson and Schijf (2011) measured the stability of REE complexes with the model siderophore DFOB and proposed that they may constitute up to 30% of the total Lu concentration at a free ligand concentration of only  $10^{-13}$  M, mostly at the expense of its carbonate species. However, their importance diminishes with decreasing atomic number, becoming minor around Gd (Figure 3, columns SW1a,b). Unless biogenic REE ligands can be explicitly identified and investigated or the speciation model verified by direct analysis (Pižeta et al., 2015), the role of organic REE complexation in seawater remains speculative and may well be underestimated.

Another potentially important but largely neglected ligand in seawater is silicate. Until recently, only one group had determined stability constants for REE complexation with silicate and only for Eu (Jensen & Choppin, 1996; Pathak & Choppin, 2006; Thakur et al., 2007). It appears that Eu forms a first- and second-order complex similar to but substantially more stable than the corresponding carbonate complexes. Based on their results, Akagi (2013) argued that (inorganic) REE speciation is dominated by silicate throughout the ocean. That would be a remarkable conclusion, upending the paradigm that carbonate is the primary inorganic REE ligand, with potentially far-reaching implications for our understanding of REE marine geochemistry. Patten and Byrne (2017) measured the stability constant ( $_{sil}\beta_1$ ) for the first-order silicate complex of Fe(III) and used a linear free-energy relation as well as a reanalysis of the data of Jensen (1994) to show that  $_{sil}\beta_1$  for Eu was too high by 1–2 orders of magnitude, which was later confirmed (Soli & Byrne, 2017). Employing a novel titration method that is much faster and able to determine both constants, the first measurements of  $_{sil}\beta_1$  and  $_{sil}\beta_2$  are now in progress for yttrium and all REEs (Schijf & Byrne, 2021). Preliminary results suggest that silicate complexation is of minor importance in seawater and does not surpass carbonate complexation even in the nutrient-rich deep Pacific Ocean (Figure 3, column SW2), although this conclusion may need to be amended for the HREE if both reactions are proportionately impeded at high pressure (Schijf & Byrne, 2021).

Terrestrial waters of low ionic strength, characteristic of rivers, lakes, and shallow aquifers, are less strongly buffered than seawater and thus have a wider range of generally more acidic pH (4–9). While the concentrations of inorganic ligands are lower than in seawater, those of metals that are strong competitors for REE complexation, including Fe, Mn, and Al, can be much higher. In addition, rivers and lakes generally contain elevated levels of dissolved organic matter (DOM), yet with very different characteristics. Finally, the main controlling variables, pH and  $PCO_2$ , can show enormous temporal variation on short timescales caused by diel photosynthesis/respiration cycles (Gammons et al., 2005). Under these conditions, carbonate complexation of the REE is commonly suppressed to various degrees, especially in waters draining silicate rocks, allowing for enhanced complexation with other ligands, such as phosphate, possibly silicate, sulfate, or even small carboxylic acids that occur in root exudates (Schijf & Byrne, 2001).

Freshwaters can have a nearly infinite variety of compositions; hence, constraining REE speciation requires direct measurement of many chemical parameters. Perhaps consequently, it has received much less attention in the literature than seawater and most of the work has focused on groundwater. Only a single example is presented here (Figure 3, column GW) (Johannesson, Stetzenbach, et al., 1996). Carbonate complexation is suppressed by the lower pH of 7 and restricted to the first-order complex. Because the concentrations of competing ligands like sulfate and phosphate are low, REE speciation is largely shifted to the free cation, comprising more than half of the total. Johannesson, Stetzenbach, et al. (1996) also present results for pH 8 and 9, with the contribution of carbonate increasing accordingly and becoming more seawater-like, although organic complexation was not considered. The influence of low pH is shown by Turner et al. (1981), who calculated REE speciation in a model river water at pH 6, where La exists as about 75% free cation and 25% complexed with sulfate, with the contribution of the carbonate complex reduced to less than 1%. In sulfate-rich waters, the contribution of the

REE–sulfate complex can become even more pronounced, as predicted by Schijf and Byrne (2004) and modeled for the acidic Canadian Colour Lake (Johannesson & Lyons, 1995), where dissolved REEs appear to be about equally divided between the free cation and the first-order sulfate complex, with a minor but significant contribution from the first-order fluoride complex, particularly for the HREEs.

Organic REE complexation has been studied much more extensively in freshwater than in seawater. In DOM-rich waters (Adebayo et al., 2018; Dia et al., 2000; Pourret et al., 2007; Tang & Johannesson, 2003), the influence of organic ligands should be quite substantial, although it is lessened below pH 5 as most of their functional groups become protonated. Contrary to the ocean, where the organic speciation of many metals appears to be controlled by a few very strong but relatively small ligands (Vraspir & Butler, 2009), the most important organic molecules in freshwater may be a diverse class of humic and fulvic acids containing myriad functional groups. More effort has been devoted to the parameterization of these polyanionic multidentate ligands in advanced speciation computer codes (Marsac et al., 2011, 2021; Milne et al., 2003; Pourret & Martinez, 2009) than to their detailed characterization or an exact determination of their stability constants. Although humic compounds are thought to affect marine metal speciation (Whitby & van den Berg, 2015), they have a different origin and structure. Terrestrial humic ligands are so large that they cross into the realm of colloids, which play a complicated part in REE behavior as they bridge the gap between dissolved and particulate species (Schijf & Zoll, 2011). One exception to the predominance of humic and fulvic acids may be the role of certain exceedingly strong manmade ligands. The polycarboxylic acid DTPA and similar compounds are used as contrast agents (CA) for magnetic resonance imaging (MRI) and discharged in large quantities bound to Gd, which, despite its stability, may be exchanged for other REEs in so-called transmetallation processes (Idée et al., 2006), globally leading to positive Gd anomalies in rivers (Rogowska et al., 2018). These contaminants are emerging in rivers, estuaries, and coastal waters (e.g., R. L. Andrade et al., 2020; Bau & Dulski, 1996a; Hatje et al., 2014, 2016; Pedreira et al., 2018), as will be discussed later on.

Hydrothermal fluids, found in the subsurface and emitted from seafloor vent systems where pressures are very high, are characterized by temperatures of 50–400°C (at  $P_{\text{sat}}$ ) or above. Their compositions are commonly very different from surface waters due to contact with ambient minerals and can be markedly enriched in weaker inorganic ligands and competing metal cations. Hydrothermal fluids generally have low levels of organic ligands and phosphate due to a lack of biological activity. Concentrations of the REEs may be quite high and saturated with regard to insoluble salts such as fluorides (Migdisov & Williams-Jones, 2007), showing unusual distribution patterns. Relevant thermodynamic data are lacking due to the experimental challenges of measuring stability constants at high temperatures and pressures. Several studies have focused on REE complexation with chloride, fluoride, and sulfate (Gammons et al., 1996; Gammons, 2002; Migdisov et al., 2008; Migdisov & Williams-Jones, 2006, 2007; Ragnarsdottir et al., 1998). These reactions are endothermic and thus strongly favored at high temperature, particularly for the high-order complexes. Wood (1990b) critically reviewed stability constants up to 350°C and  $P_{\text{sat}}$ . Haas et al. (1995) invoked a comprehensive, self-consistent data set of enthalpies and entropies to model stability constants out to 1000°C and 5 kbar. The latter paper emphasizes broad trends and may be less accurate at specific temperatures. Both use the resulting constants to calculate REE speciation as a function of pH in model hydrothermal fluids of somewhat similar composition (Figure 3, columns HF1 and HF2).

The Eu speciation of Wood (1990b) in hydrothermal fluids is entirely dominated by fluoride, consisting of about 90% of the third-order complex. Despite a higher temperature and tenfold more fluoride, only half of the La concentration of Haas et al. (1995) consists of the first-order fluoride complex, the rest being nearly equally divided among the free cation and the hydroxide and two chloride complexes. These discrepancies illustrate the troublesome sensitivity of REE speciation calculations to minor differences in conditions and solution composition, considering the present uncertainties in the thermodynamic data.

It is important to bear in mind that the examples of REE speciation presented here are only models based on thermodynamic data and not on any kind of in situ measurement. Unlike other trace metals (e.g., Pizeta et al., 2015), it is not yet feasible to measure the concentrations of free REE cations or their complexes directly. Besides a general agreement between calculated speciation diagrams and REE geochemical behavior in natural systems, we have no independent analytical confirmation of their accuracy. In other words, a speciation diagram is only as good as the model employed to derive it. The main problems that may cause speciation diagrams to be flawed are (a) inaccurate or (b) missing thermodynamic data and (c) the exclusion of important ligands or competing metals. The example of REE–silicate complexation demonstrates how inaccurate data can lead to

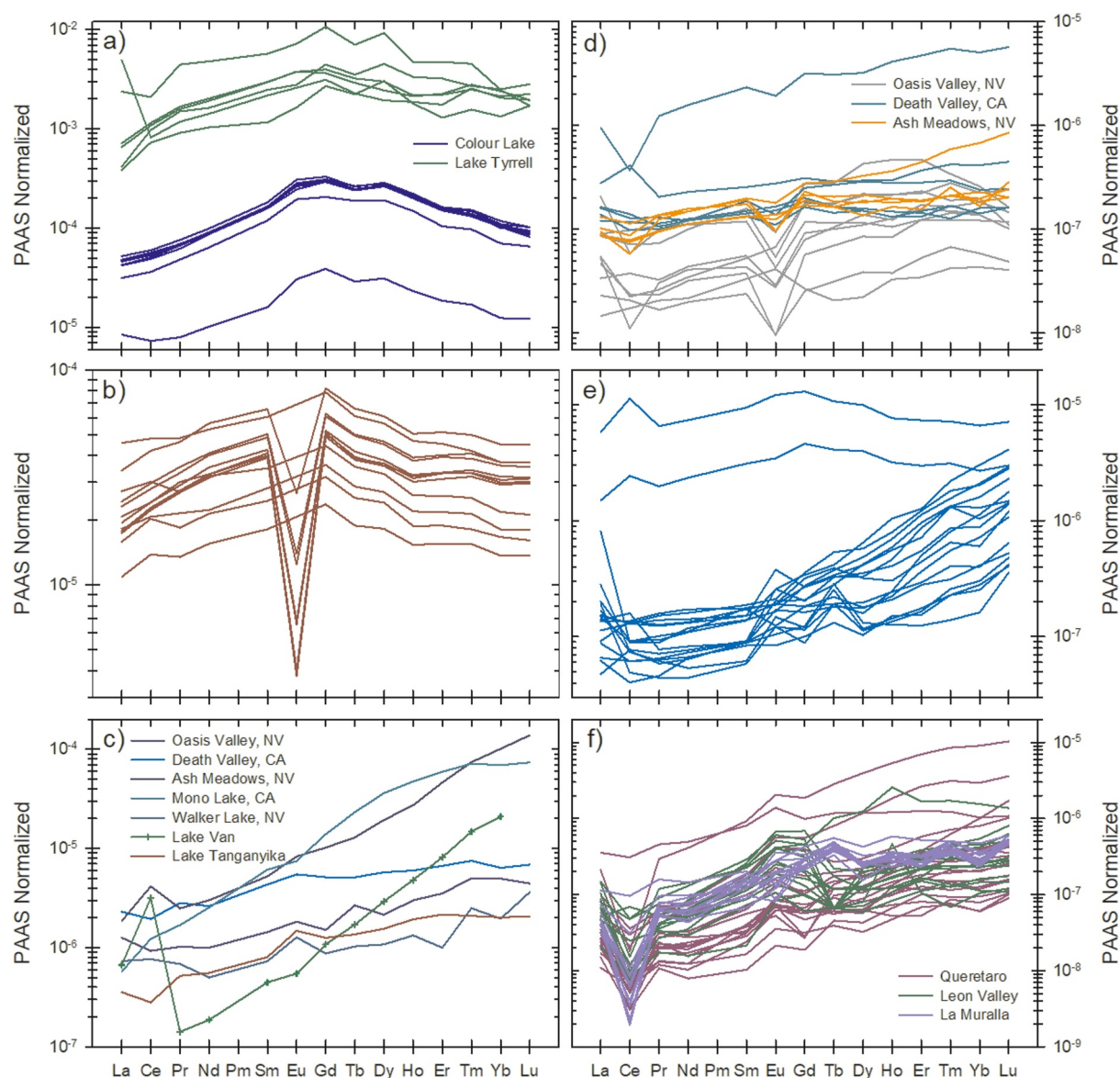
erroneous conclusions. Thermodynamic data are sorely lacking at high temperatures and pressures, particularly solubility products that are crucial wherever waters are in close contact with rocks, soils, and sediments. Most experiments are performed at standard state conditions and whereas complexation enthalpies are known for many reactions, these are commonly measured over a limited range of temperature, preventing an accurate determination of molar heat capacities (Schijf & Byrne, 2008). This hampers speciation modeling not only in hydrothermal fluids but notably at high pressure and low temperature (Lee & Byrne, 1994), reflecting conditions throughout the deep ocean. Finally, many ligands and other metals are omitted from REE speciation models because their relevance cannot be assessed from available data. This has been true for silicate and phosphate, for which stability constants have not been directly measured for most REEs. For organic compounds, key ligands in many natural waters have not even been identified. It is also true for metals in hydrothermal fluids, which can be competitive and present at high concentrations. In summary, model results should be interpreted with caution and published stability constants and speciation diagrams not always accepted at face value.

## 2. Environmental Distribution and Controlling Processes—Elements and Isotopes

### 2.1. Rivers, Lakes, and Groundwater

One of the earliest investigations of REEs in groundwaters showed that because REEs formed strong and stable aqueous complexes with chelators, they were potentially powerful tracers of groundwater-rock reactions and groundwater flow (Bigot et al., 1984). These authors reported that the adsorption and desorption behavior of the REEs was proportional to their stability constants with aqueous ligands, and that these features of REEs would lead to fractionation of the REE series during their transport along the groundwater flow paths, similar to what is observed for rivers and estuaries. Following on the study by Bigot et al. (1984), Smedley (1991) quantified the concentrations of the REEs in mildly acidic groundwaters from a granitic rock aquifer and from a metasedimentary (chiefly slate) rock aquifer in Cornwall from the southwestern United Kingdom. She demonstrated that the REE signatures of these groundwaters closely resembled the REE signatures of the specific rock types through which they flowed, further emphasizing their utility as tracers of water-rock reactions (Smedley, 1991). Moreover, she showed that characterizing the REE signature of groundwaters can provide a means of tracing groundwater flow based on aquifer composition, which has since been the theme of several later studies (Johannesson, Stetzenbach, & Hodge, 1997; Johannesson, Stetzenbach, Hodge, Kreamer, & Zhou, 1997; Tweed et al., 2006). Such an approach is essentially identical to the use of strontium isotope ratios in groundwaters (Lyons et al., 1995; Ojiambo et al., 2003).

To a first approximation, the input-normalized REE signature of groundwaters and river waters appears to reflect the results of biogeochemical reactions between the waters and REE bearing minerals in the aquifer rocks or source rocks during chemical weathering, as well as clay minerals and Fe-Mn oxides/oxyhydroxides coating these and other minerals (Chevis, Johannesson, Burdige, Tang, et al., 2015; Goldstein & Jacobsen, 1988b; Smedley, 1991; Tang & Johannesson, 2005; Willis & Johannesson, 2011). Here, weak acids such as carbonic acid and organic acids, some likely produced by microbes, appear to be responsible for mobilizing REEs during chemical weathering reactions (Banfield & Eggleton, 1989; Brantley et al., 2001; Cervini-Silva et al., 2005; Nesbitt, 1979; Taunton et al., 2000; Voutsinos et al., 2022). The relative distributions of the REE mobilized by these biogeochemical reactions can then be further fractionated by the combined impacts of aqueous solution and surface complexation (Byrne & Liu, 1998; Elderfield et al., 1990; Goldstein & Jacobsen, 1988b; Johannesson et al., 2005; Sholkovitz, 1978; Willis & Johannesson, 2011). Specifically, aqueous complexation of REE with dissolved ligands like carbonate anions and natural organic ligands preferentially stabilize the HREE in solution by lowering the aquo ion activity, for example,  $a_{\gamma_{b^{3+}}}$ , thus impeding surface complexation reactions of the HREE compared to the LREE (Byrne & Kim, 1990; Cantrell & Byrne, 1987; Marsac et al., 2010; Pourret et al., 2007). These same solution and surface complexation reactions are also thought to be responsible for the fractionation of the REEs in rivers, estuaries, and the ocean (Byrne & Liu, 1998; Elderfield et al., 1990; Goldstein & Jacobsen, 1988a, 1988b; Hoyle et al., 1984; Schijf et al., 2015). Moreover, the dissolved inorganic and organic ligands in weathering solutions preferentially complex with the HREEs, effectively removing them from the site of active weathering, whereas the LREEs are preferentially retained by adsorption or incorporation in secondary clay minerals or phosphate minerals formed during incongruent chemical weathering (Banfield & Eggleton, 1989; Duddy, 1980; Schau & Henderson, 1983). Colloids are also likely to be important in elevating LREE



**Figure 4.** Rare Earth Elements (REE) patterns of lake and groundwater samples normalized to PAAS. (a) acid waters ( $3.6 \leq \text{pH} \leq 4.7$ ) from Colour Lake (Nunavut, Canada) and acid groundwaters (pH 3.1) beneath Lake Tyrrell, Victoria, Australia; (b) acidic, organic-rich blackwaters of the Great Dismal Swamp in Virginia, USA; (c) alkaline lake waters from the western Great Basin of the USA (Goose, Summer, Abert, Mono, and Walker Lakes;  $9 \leq \text{pH} \leq 10$ ) as well as from Lake Van in Turkey (pH 9.6) and Lake Tanganyika (pH 8.75) in East Africa; (d) groundwaters from Oasis Valley, Ash Meadows, and Death Valley in southern Nevada and eastern California, USA; (e) groundwaters from southern Saskatchewan, Canada; (f) groundwaters from the states of Guanajuato and Querétaro in México. Note that the ordinate varies between panels owing to the large differences in REE concentrations as a function of pH. Data from Fee et al. (1992), Möller and Bau (1993), Johannesson and Lyons (1994, 1995), Johannesson, Stetzenbach, Hodge, Kreamer and Zhou (1997), Johannesson et al. (1994, 1999, 2000, 2005, 2006), Barrat et al. (2000), and Johannesson and Hendry (2000).

concentrations in rivers (Merschel et al., 2017) and some groundwaters (Brewer et al., 2022; Goldstein & Jacobsen, 1988b; Ingri et al., 2000; Smedley, 1991; Stolpe et al., 2013).

Following Smedley (1991), Fee et al. (1992) investigated the REEs in acid, hypersaline groundwaters from Victoria, Australia, and Gosselin et al. (1992) studied the REEs in chloride-rich acid groundwater from Texas, USA. Both investigations further illustrated the utility of the REE to trace different groundwater sources and identify possible water-rock reactions. For example, Fee et al. (1992) used differences in the shale-normalized REE patterns to distinguish between three different types of groundwaters beneath an Australian dry lake (Figure 4a) that included: (a) regional groundwaters exhibiting the highest REE concentrations, (b) an

intermediate “transitional” groundwater with lower REE concentrations, and (c) a reflux brine located beneath both the regional and “transitional” groundwaters. In contrast, Gosselin et al. (1992) showed that acid groundwaters that flowed through arkosic rocks had flat, shale-normalized patterns that closely resembled the REE patterns of these rocks, whereas groundwaters that flowed through carbonate rocks and had reacted with MREE-enriched Fe-Mn oxides/oxyhydroxide coatings on the carbonate minerals and/or secondary vug-filling minerals had MREE enriched patterns. Similar MREE-enriched shale-normalized patterns of acid waters were observed in the Canadian High Arctic (Figure 4a) that also appear to reflect water-rock reactions with MREE enriched Fe(III)/Mn(IV) oxides/oxyhydroxides within the local bedrock and associated sediments (Johannesson & Lyons, 1995; Johannesson & Zhou, 1999). In contrast, the shale-normalized MREE-enriched patterns of surface waters from the Great Dismal Swamp in Virginia likely reflect preferential complexation of MREE with natural organic matter (Johannesson et al., 2014; Marsac et al., 2010; Tang & Johannesson, 2010) (Figure 4b).

Following these earlier studies, the REEs were successfully employed to trace groundwater flow, mixing, and mineral dissolution reactions in aquifers from Tennessee, southern Nevada, and Massachusetts in the USA as well as in Victoria, Australia (Bau et al., 2004; Johannesson et al., 1999; McCarthy et al., 1996; Tweed et al., 2006, among many others). In a series of papers from the mid-to late 1990s, Johannesson and colleagues reported that the input-normalized REE patterns of groundwaters discharging from regional carbonate aquifers in southern Nevada and eastern California differed from those abstracted from felsic volcanic rock aquifers from the same geographic region (Johannesson, Lyons et al., 1996; Johannesson, Stetzenbach et al., 1996; Johannesson, Stetzenbach, Hodge, Kreamer, & Zhou, 1997; Stetzenbach et al., 2001; Figure 4d). The REE fractionation patterns were consistent with groundwaters issuing from carbonate springs in Death Valley National Park, California, having originated by mixing of locally recharged groundwaters with groundwaters from the Pahrnagat Valley ~150 km to the north (Johannesson, Stetzenbach, & Hodge, 1997; Johannesson, Stetzenbach, Hodge, Kreamer, & Zhou, 1997). These conclusions were supported by stable water isotope ratios (i.e.,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) and uranium-series isotopes (i.e.,  $^{234}\text{U}/^{238}\text{U}$ ) of regional groundwaters and hydrologic head levels as well as the orientation of several major faults in southern Nevada and eastern California (Farmer, 1996; Johannesson, Stetzenbach, & Hodge et al., 1997; Lacznik et al., 1996).

Although the application of the particle-reactive REE to trace groundwater flow seems counterintuitive, the inclusion of aqueous complexation modeling helped facilitate a more mechanistic understanding of how the REE could exhibit pseudo-conservative behavior over groundwater flow paths of several tens of kilometers. Specifically, aqueous complexation modeling suggests that the REEs are chiefly complexed with carbonate ions in circumneutral pH groundwaters, and further that the dicarbonato complex (i.e.,  $\text{Ln}(\text{CO}_3)_2^-$ ) accounted for substantial fractions of dissolved HREEs, especially when pH exceeded ~7.5 (Johannesson et al., 2005; Johannesson, Stetzenbach, et al., 1996). The dicarbonato complex is not as strongly adsorbed as other REE species onto surface sites within the local aquifer, preferring instead to remain in solution relative to the LREE, which primarily formed positively charged carbonato complexes (i.e.,  $\text{LnCO}_3^+$ ) (Johannesson, Stetzenbach, & Hodge, 1997; Tang & Johannesson, 2005) (Figure 4f). These findings are reminiscent of the early work by Bigot et al. (1984). Hence, these and other investigations underscored the importance of controls that aqueous complexation, and hence solution composition, place on the fate and transport of REEs in groundwater flow systems (Rönnback et al., 2008; Tweed et al., 2006).

As with other reactive metals, the geochemistry of the REEs in natural terrestrial waters is closely coupled to pH, exhibiting an inverse relationship such that REE concentrations increase with decreasing pH (Elderfield et al., 1990; Goldstein & Jacobsen, 1987, 1988b). Hence, some of the lowest measured REE concentrations have been reported for circumneutral pH groundwaters where individual REEs such as Yb can be 5- to 10-fold lower than in seawater (Kreamer et al., 1996; Stetzenbach et al., 1994) (Figures 4d–4f). At higher pH values REE concentrations tend to increase such that alkaline, saline lakes with pH  $\approx$  10 like Mono Lake in eastern California, Lake Abert in eastern Oregon, Lake Van in Turkey (Figure 4c), and Lakes Aha and Hongfeng in China (data not shown) are strongly enriched in the REE, and especially the HREE (Barrat et al., 2000; Johannesson et al., 1994; Johannesson & Lyons, 1994; Möller & Bau, 1993; Z. L. Wang et al., 2013). Indeed, not only are the input-normalized fractionation patterns enriched in HREE over the LREE in Mono and Abert Lakes, but the measured concentrations of individual HREE are also higher than those for individual LREE (Johannesson et al., 1994; Johannesson & Lyons, 1994) (Figure 4c). The increase in HREE concentrations is thought to reflect stabilization of HREE in these lake waters owing to the formation of strong carbonate complexes, particularly dicarbonato complexes (Johannesson & Lyons, 1994; Möller & Bau, 1993).



Terrestrial waters with  $\text{pH} \geq 10$  appear to be rare and largely confined to regions where low-temperature serpentinization is ongoing (e.g., Bruni et al., 2002; Chavagnac et al., 2013; Leong & Shock, 2020, and references therein). To the best of our knowledge, only one study reports REE concentrations in hyperalkaline, high pH groundwaters ( $\text{pH} \geq 11$ ), which do not exhibit enrichment in the HREE like those reported for alkaline, saline lake waters, and instead have flat to mildly LREE enriched, shale normalized REE patterns (Zwicker et al., 2022). The lack of strong, HREE enrichment in these hyperalkaline groundwaters likely reflects the low dissolved inorganic carbon concentrations in which alkalinity is dominated by hydroxyl ions and not carbonate ions.

Therefore, although some terrestrial waters have REE distributions that closely reflect the REE distributions of local rocks/sediments/minerals (e.g., Banner et al., 1988; Gosselin et al., 1992; Smedley, 1991), others such as alkaline, saline lakes and circumneutral pH groundwaters commonly have highly fractionated, input-normalized REE patterns compared to both shale composites and local rocks (Figures 4c–4f). In many instances, the input normalized REE fractionation patterns of circumneutral pH groundwaters resemble those of seawater, namely middle to HREE enrichments relative to the LREE, negative Ce anomalies, and even superchondritic Y/Ho ratios (Bau et al., 2004; Chevis, Johannesson, Burdige, Cable, et al., 2015; Johannesson et al., 2005, 2006; Johannesson et al., 2011) (Figure 4f). These observations are consistent with a model that REE fractionation patterns evolve along groundwater flow paths as groundwaters react with the aquifer rocks/sediments and biogeochemical processes such as anaerobic microbial respiration and chemical weathering modify the groundwater chemistry and pH.

A conceptual model advanced by Johannesson and collaborators (Johannesson et al., 1999, 2005) and further supported by other researchers (Alibo & Nozaki, 1999; Tang & Johannesson, 2005; Tweed et al., 2006) is that REEs are initially mobilized in groundwater systems near the recharge area (e.g., Nesbitt, 1979). These infiltrating waters are commonly saturated with respect to atmospheric  $\text{CO}_2$  and become even more acidic as they pass through the soil zone owing to  $\text{CO}_2$  generated by respiring plants (e.g., roots) and soil microbes. As a result, infiltrating soil waters with pH values as low as 4 are not uncommon. Such acidic aqueous fluids can mobilize REEs in relative distributions that closely mimic the most environmentally labile mineral fractions, including coatings on the aquifer minerals and/or organic matter phases within the soil zone of the recharge area (Duvert et al., 2015; Omonona & Okogbue, 2017; Pédrot et al., 2015; Tang & Johannesson, 2005). As the initially acidic groundwater flows down a gradient along the flow path, it continues to react with minerals within the aquifer materials generating  $\text{HCO}_3^-$ , as silicate and carbonate minerals dissolve, and raising the groundwater pH. Increases in pH are partly buffered by  $\text{CO}_2$  produced within the aquifer by respiring bacteria that use terminal electron acceptors such as Fe(III)/Mn(IV) oxides/oxyhydroxides and  $\text{SO}_4^{2-}$  to oxidize organic carbon and other reductants. However, because many groundwater flow systems are highly oligotrophic, chemical weathering of minerals within these flow systems commonly plays a dominant role, driving pH increases to values that can exceed 9 (Chapelle & Knobel, 1983; Flynn et al., 2012; Lovley & Chapelle, 1995; Park et al., 2006). As groundwater pH rises above 7, the combination of aqueous and surface complexation further fractionates the REEs by preferentially stabilizing HREEs in solution as  $\text{Ln}(\text{CO}_3)_2^-$  complexes, contrary to the LREEs, which are preferentially adsorbed onto mineral surface sites (Biddau et al., 2009; Carr et al., 2016; Johannesson et al., 2005; Tang & Johannesson, 2006; Willis & Johannesson, 2011). These processes act to enrich the input-normalized HREE values in groundwaters and deplete the input-normalized values of the LREE, leading to HREE enriched input-normalized fractionation patterns. Similar competition between aqueous complexation and surface complexation also modifies river water REE distributions, commonly leading to HREE-enriched shale-normalized patterns (Byrne & Liu, 1998; Elderfield et al., 1990; Hoyle et al., 1984; Sholkovitz, 1995).

Submarine groundwater discharge (SGD) has been recognized as an important source of REEs to the coastal ocean (Duncan & Shaw, 2003; Johannesson & Burdige, 2007). Diagenetic REE flux to coastal waters appears to be related to the biogeochemical degradation of organic carbon of terrestrial origin (Duncan & Shaw, 2003). Moreover, it was hypothesized that SGD may be an important component of the missing Nd flux to the ocean necessary to balance the ocean Nd budget and address the “Nd paradox” (Goldstein & Hemming, 2003; Johannesson & Burdige, 2007). Because SGD occurs along ocean margins, it is likely to be part of the “Boundary Exchange” process.

Several site-specific investigations of the REE and Nd isotopes revealed substantial terrestrial SGD fluxes to coastal waters that ranged from 1 to 3 mmol Nd day<sup>-1</sup> along the Kona Coast of Hawaii up to 26 mmol Nd day<sup>-1</sup> within the Pettaquamscutt River estuary in Rhode Island (Chevis et al., 2021; Chevis, Johannesson, Burdige,

Tang, et al., 2015; Johannesson et al., 2011, 2017). At the Florida and Rhode Island sites, the terrestrial SGD REE flux was of the same magnitude as local stream water fluxes. The magnitude of the terrestrial SGD Nd fluxes reported for the Indian River Lagoon (Florida), the Pettaquamscutt River estuary, and the Kona Coast are comparable to those for a barrier island along the coast of Germany (5.03 mmol Nd day<sup>-1</sup>; Paffrath et al., 2020) and the Bay of Bengal near the Sankarabarini River in southern India (25.7 mmol Nd day<sup>-1</sup>; Ponnunani et al., 2022), but several orders of magnitude lower than found along the coast of Jeju Island, South Korea (57.5–219 mol Nd day<sup>-1</sup>; I. Kim & Kim 2011, 2014). Molina-Kescher et al. (2018) estimated SGD fluxes from Tahiti, another basaltic island in the South Pacific, which were also similar in magnitude to those reported for the Kona Coast of Hawaii (Johannesson et al., 2017). Hence, the substantially higher SGD fluxes of Nd reported from Jeju Island are perplexing but appear to reflect the remarkably high REE concentrations measured in coastal groundwaters from this basaltic island.

To the best of our knowledge, the first SGD Nd isotope compositions and fluxes were reported by Chevis et al. (2021) for the Indian River Lagoon system of Florida's Atlantic coast. These authors concluded that biogeochemical reactions occurring in the subterranean estuary, namely microbially facilitated reductive dissolution of Fe(III) oxides/oxyhydroxides coating the sandy, quartz-rich sediments, was the chief source of Nd and hence REE to these coastal waters. More specifically, labile marine-sourced organic matter that circulates through the subterranean estuary fuels microbial respiration of the Fe(III) oxides/oxyhydroxides, which releases both Fe (II) and adsorbed REEs into solution (Roy et al., 2010, 2011, 2013). Once mobilized, Fe(II) and REEs flow upward with advecting groundwater. Ferrous iron precipitates as Fe sulfide minerals in the shallow sediments directly below the seafloor, whereas the REEs are discharged into the overlying coastal surface waters of the Indian River Lagoon (Chevis et al., 2021). These researchers estimated that the total SGD flux of Nd (i.e., terrestrial and recirculated marine flux) was on the order of 200 mmol day<sup>-1</sup> and had an  $\epsilon_{\text{Nd}}$  value of  $-6.5$ . Hence, the SGD flux accounts for about half of the total surface water flux of Nd to the coastal ocean (i.e., ca. 400 mmol Nd day<sup>-1</sup>) from the studied portion of the Indian River Lagoon, and furthermore, the Nd isotope composition of this total surface flux was identical to the total SGD flux, that is,  $\epsilon_{\text{Nd}}(0) = -6.47 \pm 0.16$  (Chevis et al., 2021).

In summary, research into the REE in terrestrial waters over the past 30 years has helped illuminate the mechanisms that mobilize these trace elements from geological materials as well as the biogeochemical processes that fractionate the REE in natural waters. Some of the important processes that have been identified include differential or incongruent weathering of minerals, aqueous complexation with inorganic and natural organic ligands, solubility constraints set by sparingly soluble REE phosphate, carbonate, and hydroxide minerals, and sorption of REE onto metal oxide/oxyhydroxides and clay minerals. Future research is still required to more quantitatively understand the origins of the myriad of input-normalized REE fractionation patterns observed for terrestrial waters (Figure 4), develop models that can simulate the fate and transport of REEs in aquifers, and how recently identified methanotrophs that can use or even require lanthanides in an alternative methanol dehydrogenase to metabolize methane (e.g., Daumann, 2019) may also influence REEs in terrestrial waters.

## 2.2. Land-Ocean Interfaces

### 2.2.1. Estuaries

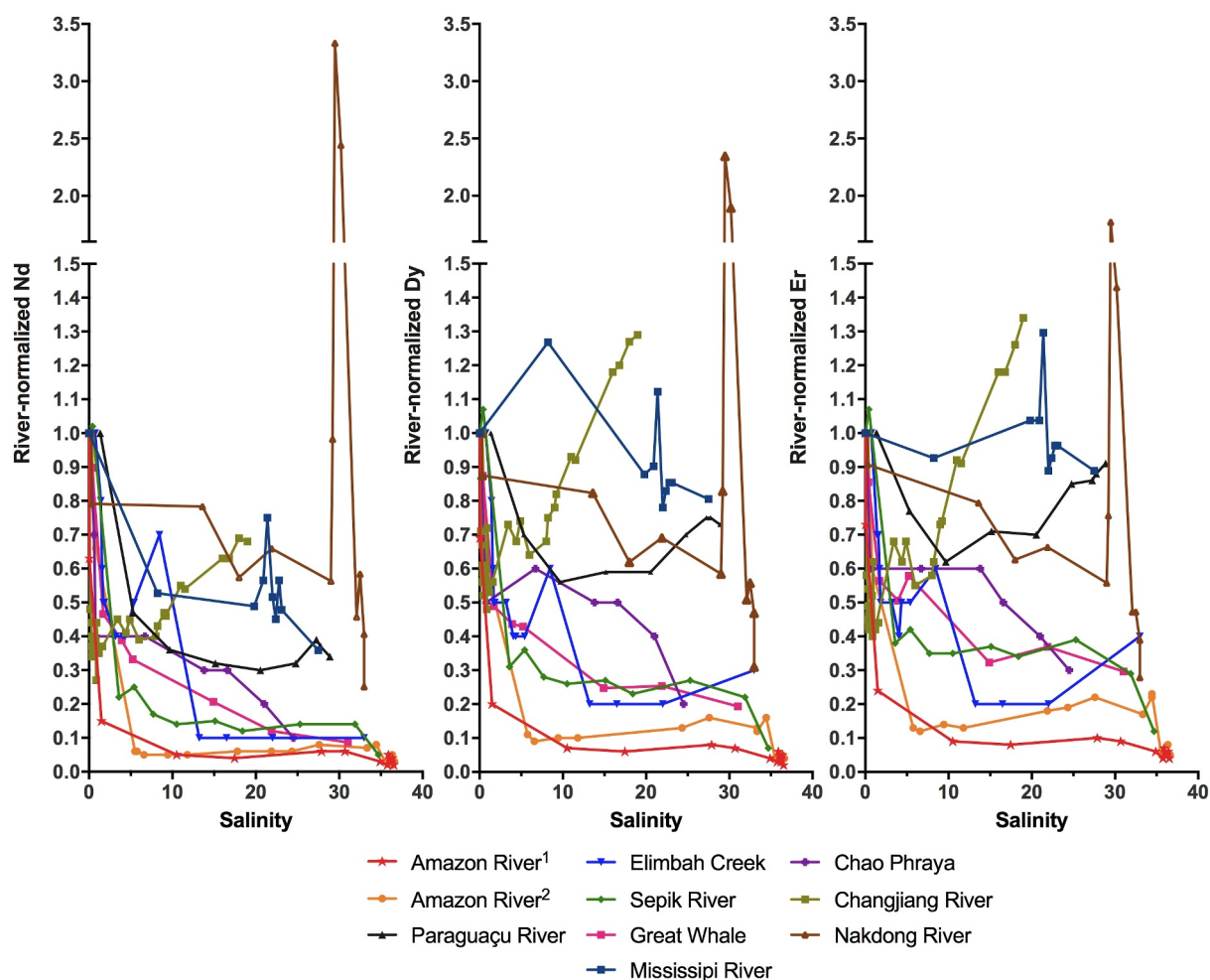
Estuarine processes have long been recognized as of high importance in modifying the input of dissolved and particulate riverine loads of inorganic and organic matter to coastal waters and ultimately the ocean (Eckert & Sholkovitz, 1976; Lawrence & Kamber, 2006; Sholkovitz, 1978). The study of REE and Nd isotope composition in river-suspended material has shown that the general assumption that they are not fractionated during Earth surface processes may be overstated (Bayon et al., 2015). Nd isotopic analysis on different grain-size fractions may display distinct compositions, attributed to the preferential breakdown of young volcanic material, while high REE mobility could occur during weathering under all types of climate, leading to significant decoupling of Nd isotopes between parent rocks, soils, and river waters (Bayon et al., 2015 and references therein).

It is important to understand the physico-chemical processes governing the behavior of trace metals during estuarine mixing of river and seawater to estimate the impact of estuarine removal on the trace element budget of the world's oceans. Following the removal of iron and other trace elements through the flocculation of inorganic and organic nanoparticles and colloids, dissolved REEs experience substantial removal in the estuarine zone, exhibiting non-conservative behavior along the salinity gradient (e.g., R. L. Andrade et al., 2020; Elderfield

et al., 1990; Goldstein & Jacobsen, 1988a, 1988b; Rousseau et al., 2015; Sholkovitz et al., 1978, 1995; Sholkovitz & Szymczak, 2000; Sholkovitz, 1993). Hoyle et al. (1984) demonstrated a significant removal of estuarine REEs from solution, mainly in the low salinity range (0–5 salinity), concluding that REEs are strongly associated with organic matter and that REE removal occurs due to the flocculation of iron-organic matter colloids. These authors also noted that Ce behaved coherently with La and Nd, implying that the Ce anomaly is not generated due to estuarine mixing. Similarly, Sholkovitz (1993) observed over 90% removal of REEs in the Amazon estuary within a salinity range of 0–6.6, attributing this phenomenon to the coagulation of riverine colloids. However, in the same study, a slight increase in REE concentrations was observed within the salinity range of 6.6–34, resulting from the release of REEs from sediments and suspended particles or the heterogeneous distribution of REE concentrations within the Amazon River plume. Conversely, Merschel et al. (2017) found REE conservative behavior in Rio Negro, Brazil. According to the authors, in this system, the nanoparticles and colloids are mainly humic and fulvic acids that during estuarine mixing precipitate removing trace elements including REE from the solution (Fox, 1983; Sholkovitz, 1978; Zhou et al., 1994). Other studies have also indicated a slight increase in REE concentrations at high salinities (Elderfield et al., 1990; Sholkovitz & Szymczak, 2000). Additionally, a pattern of HREE (heavy REE) > MREE (medium REE) > LREE (light REE) release has been observed at higher salinities, which is the reverse of the order observed at lower salinities (e.g., R. L. Andrade et al., 2020; Rousseau et al., 2015; Sholkovitz, 1993). Figure 5 illustrates this variability pattern, showcasing the differential fractionation of REEs along the salinity gradient in various estuarine systems. The increase in REE concentrations from mid to high salinity starts at lower salinities for the HREE (between 10 and 15) than for the MREE (between 10 and 25) and the LREE (between 15 and 25) (Figure 5). Sholkovitz (1995) reported that REE fractionation accompanies the removal of the dissolved phase during the coagulation of organic iron oxide colloids, to which REEs are strongly associated, and is also a result of the release of REEs from river and estuarine particles with increasing salinity. Several dominant factors of REE speciation and fractionation in estuaries have been identified, considering total organic carbon (TOC) as the most important factor for REE speciation and bioavailability in estuarine sediments (Chakraborty et al., 2011). Although more than half of REEs were bound to inert complexes and were not bioaccessible, about 20%–30% were associated with TOC. Furthermore, C. Zhang et al. (1998) considered that REEs were fractionated as iron and manganese compounds (9%–16%), carbonates (3%–6%), and water-soluble (1%–11%) fractions. In the Rhine-Meuse estuary, Moermond et al. (2001) report that dissolved REEs are mainly complexed with carbonates and dissolved organic matter, pointing to a decrease in the relative abundance of the ionic form  $\text{LnCO}_3^+$  from La to Lu, while the relative abundance of  $\text{Ln}(\text{CO}_3)_2^-$  increases.

Fluvial and groundwater inputs are important sources of terrestrial REEs to the ocean, although other sources (e.g., dust deposition and deep-sea benthic flux) likely play a significant role (e.g., Abbott, 2019; Abbott, Haley, & McManus, 2015; Byrne & Sholkovitz, 1996; Duncan & Shaw, 2003; Haley et al., 2017; Johannesson & Burdige, 2007; Sholkovitz, 1993), as will be discussed. Globally, the riverine shale-normalized patterns of REEs are diverse, evidencing light, medium, and heavy REE enrichments, with concentrations ranging across three orders of magnitude. In contrast, the normalized marine REE pattern is globally more consistent and characterized by a depletion of LREE relative to HREE, an enrichment of La, and a depletion of Ce (Byrne & Liu, 1998; Elderfield & Greaves, 1981; Elderfield, et al., 1988, 1990; Garcia-Solsona & Jeandel, 2020; Lawrence & Kamber, 2006; Molina-Kescher et al., 2014; Molina-Kescher et al., 2018; Osborne et al., 2015; Pham et al., 2019; Siddall et al., 2008; X. Y. Zheng et al., 2016).

The distribution of REEs in estuarine sediments is influenced by various early diagenetic processes, particularly co-precipitation into Fe-Mn oxides/oxyhydroxides, redox conditions in the water column, the composition of terrigenous sources, and anthropogenic inputs (Brito, Prego et al., 2018). Several authors have studied the geochemical cycling of the REEs in estuaries, which can be used as geochemical indicators associated with the origin of the sediments (Babu et al., 2021; Censi et al., 2005; de Chanvalon et al., 2016; de Freitas et al., 2021; Hannigan et al., 2010; Merschel et al., 2017; Munksgaard et al., 2003; Prego et al., 2009; Silva-Filho et al., 2011). Bayon et al. (2015) confirmed earlier assumptions that river sediments do not generally exhibit significant grain-size dependent Nd isotopic variability, although, a subtle decoupling of Nd isotopes between clays and silts was identified in a few major river systems, suggesting that preferential weathering of volcanic and/or sedimentary rocks relative to more resistant lithologies may occur in river basins, possibly leading locally to Nd isotopic decoupling between different size fractions. Bayon, Douglas, et al. (2020) also examine REE and neodymium isotopic compositions in grain-size fractions from river-suspended matter in the Murray-Darling Basin and a marine sediment core off the coast of Australia, showing that significant size-dependent geochemical decoupling



**Figure 5.** Concentrations of Nd (LREE), Dy (MREE), and Er (HREE) normalized to the REE concentrations of the freshwater endmember along the salinity gradient in several estuarine systems (adapted from R. L. Andrade et al., 2020). Data from: Amazon River<sup>1</sup> (Rousseau et al., 2015), Amazon River<sup>2</sup> (Sholkovitz, 1993), Paraguaçu River (R. L. Andrade et al., 2020), Elimbah Creek (Lawrence & Kamber, 2006), Sepik River (Sholkovitz & Szymczak, 2000), Great Whale River (Goldstein & Jacobsen, 1988a), Mississippi River (Adebayo et al., 2018), Chao Phraya River (Nozaki et al., 2000), Changjiang River (Z. L. Wang & Liu, 2008), and Nakdong River (T. Kim et al., 2020). The Nakdong River presents a sharp rise in REE normalized concentrations around salinity 30 due to the influence of wastewater discharge from a wastewater treatment plant.

can occur in river systems, with a preference for volcanic origin for fine-grained inorganic particles transported by river systems and suggesting that river sediment discharge is accompanied by the export of fine-grained volcanogenic particles to the ocean, potentially impacting marine productivity.

Furthermore, numerous studies have focused on the mobility of REEs between dissolved and particulate fractions in estuaries impacted by acid mine drainage (AMD) inputs (Brito, Cesário et al., 2020 and references therein). AMD is characterized by low pH and high concentrations of dissolved elements, including trace metals such as REEs, which can alter the fractionation of REEs in the receiving environment. Because estuaries act as transition zones, acidic REE-rich waters interact with alkaline ocean waters, leading to complex processes that control the geochemical characteristics of dissolved and particulate REEs. Lecomte et al. (2017) found that REE are retained in minerals formed from the interaction of AMD with seawater (pH > 6), resulting in increased concentrations of REE in estuarine sediments. Conversely, at low pH values (3–3.5), REEs are released into the solution. In the case of the Huelva estuary (southwestern Spain), a study revealed higher REE concentrations at low pH values in the river, whereas as pH increased in the estuary, these metals were reabsorbed onto insoluble salts and Fe oxide/oxyhydroxides (Lecomte et al., 2017). Similar behavior has been observed in other AMD-related estuarine systems (Ayora et al., 2015; Bonnail et al., 2017; Pérez-López et al., 2010; Prudêncio et al., 2015; Sharifi et al., 2013; Soyol-Erdene et al., 2018).

Estuarine sediments associated with salt marshes (Brito, Prego et al., 2018; López-González et al., 2012; Morgan et al., 2016; S. Wang et al., 2015), mangroves (de Freitas et al., 2021; Kumar et al., 2014; Morgan et al., 2016; Sappal et al., 2014; Silva-Filho et al., 2011), and seagrasses (de Sena et al., 2022) accumulate high amounts of fine-grained particles rich in metals, including REE. The chemical zonation of sediments plays a crucial role in the distribution of these elements between solid particles and pore waters (e.g., Berner, 1980). Because permeable sediments are a major feature in estuaries due to the presence of benthic organisms, plants, and different particles in nature, these sedimentary environments may act as a source of solutes (e.g., metals, nutrients, and organic complexes). Rivers were once thought to be the main source of REEs (Goldstein & Jacobsen, 1988b) to coastal zones, but recent studies have suggested that submarine groundwater discharges (SGD) also act as an additional source of LREE and MREE, but a sink for HREE (Chevis, Johannesson, Burdige, Tang, et al., 2015; Johannesson & Burdige, 2007; Johannesson et al., 2011; Tachikawa et al., 2003). High REE concentrations in SGD are suggested to be linked to the degradation of REE-rich relict terrestrial organic carbon and the reduction of Fe-oxides under anoxic conditions in sediments (Chevis, Johannesson, Burdige, Tang, et al., 2015; Johannesson et al., 2011; Duncan & Shaw, 2003).

In sandy subtidal areas, advection and diffusion are the main processes that transport solutes across the sediment-water interface. Otherwise, in muddy or muddy-sandy submerged sediments, diffusion becomes the primary transport mechanism across this interface, leading to vertical fluxes. The intricate interplay of biogeochemical cycles involving iron (Fe) and manganese (Mn) governs the fluxes of REEs from sediments to the water column (Adebayo et al., 2020; Schijf et al., 1995). Adebayo et al. (2020) showed that the strong concentration gradient between pore waters and the overlying waters results in an upward diffusive flux of REEs into the estuarine water column. Similar findings were reported by Sholkovitz (1992) in the Chesapeake Bay, USA; and Weltje et al. (2002) in the catchment area of the Rhine and Meuse rivers (The Netherlands). The upward flux of REEs from pore waters is accompanied by fractionation along the REE series and a preferential input of Ce relative to other trivalent REE neighbors (Sholkovitz, 1992).

In summary, estuarine processes are vital in altering the input of dissolved and particulate riverine loads into coastal and oceanic waters. Specifically, dissolved REEs display non-conservative behavior along the salinity gradient, reflecting the influence of factors such as salinity, organic carbon and particle nature on REE distribution and fractionation within estuaries. Additionally, the transport mechanisms of REE across sediment-water interfaces and the fluxes of REE from sediments to the water column underscore the intricate interplay of biogeochemical cycles involving iron and manganese.

### 2.2.2. Vegetated Coastal Ecosystems: The Plant-Soil System

During the process of weathering, REEs, together with other trace elements, are gradually released from mineral structures and can take various forms. They may enter solution, become retained on the surfaces of soil particles, or form complexes with organic matter, carbonates, phosphates, and/or other sedimentary phases (such as oxides/oxyhydroxides of Fe and Mn) (Gonzalez et al., 2014; Khan et al., 2017).

In vegetated coastal ecosystems (VCE) like saltmarshes, seagrasses, and mangroves, plants thrive in waterlogged and anoxic soil conditions. The root systems of these plants disrupt the chemical zonation of the soil (Vale & Sundby, 1998), leading to heterogeneous patterns of redox conditions (Sundby et al., 2003). The chemistry of the waterlogged anoxic soils is primarily influenced by Fe, Mn and S, which change with plant activity and the annual cycle of root growth and decay. This is significant because the speciation of sedimentary Fe and Mn is known to influence the cycling of REEs (Quinn et al., 2006), including their labile forms (Brioschi et al., 2013; Z. Huang et al., 2023; Ramos et al., 2016).

During tidal cycles, the excursion of water in VCE with the ebb and flood periods facilitates the exchange of solutes between the soil and the overlying water (e.g., Caetano et al., 1997; Huettel et al., 1998). Several studies have demonstrated upward advection fluxes of solutes from intertidal flat sediments to the water column, including nutrients (Ospina-Alvarez et al., 2014; Rocha, 1998) and redox-sensitive elements and trace metals (Caetano et al., 1997; Taillefert et al., 2007). Similar observations have been made in saltmarsh soils (Santos-Echeandía et al., 2010). Bioturbation of saltmarsh soils may promote the formation of Fe and Mn oxides/oxyhydroxides, which scavenge REEs through adsorption and/or coprecipitation. In saltmarshes of South Brazil, it seems that bioturbation plays a role in Ce redox chemistry, leading to positive Ce anomalies in core soils (L. Costa, Johannesson, et al., 2021). Although physical processes such as bioturbation and dredging can also

influence the exchange of REEs across the sediment-water interface (L. Costa, Johannesson, et al., 2021; Johannesson et al., 2011; Mirlean et al., 2020; Schaller, 2014), this topic has been understudied.

In VCE, the water column height is typically low, and episodes of wind can lead to sediment resuspension in shallow areas. This resuspension process can induce changes in the sorption equilibrium of solutes (Simon, 1989). The estuarine environment, with its dynamic nature, has a substantial impact on the speciation, solubility, distribution, and fluxes of various metal species including REEs. However, there is a lack of comprehensive studies that assess the spatial and temporal distribution of REEs and their sources and cycling within the complex estuarine—vegetated coastal ecosystems (de Freitas et al., 2021).

In many of these vegetated environments, the salinity gradient plays a role in promoting flocculation and precipitation reactions, similar to what is observed in estuaries and groundwaters. These processes facilitate the exchange of REEs between dissolved and particulate forms. During these processes, dissolved REEs are often removed, particularly in low salinity waters, due to salt-induced coagulation of colloids. This leads to fractionation, with a preferential removal of LREE over MREE and HREE (L. Costa, Johannesson, et al., 2021; Hoyle et al., 1984). L. Costa, Johannesson, et al. (2021) demonstrated an enrichment of LREE over HREE in sediments from the freshwater and brackish sections of the Patos lagoon system (Brazil), compared to sediments influenced by seawater, which exhibited a flatter REE profile.

Marshes, mangroves, and seagrass plants have the ability to mobilize and store metals within the sediments, surrounding roots, and belowground tissues (Caetano et al., 2008; L. Costa, Johannesson, et al., 2021; L. Costa, Mirlean, et al., 2021; de Sena et al., 2022). Although extensive research has been conducted on the mobilization and storage of first row transition metals and other traditional “toxic metals” such as Cu, Cd, and Hg (see Weis & Weis, 2004 for a review), investigations focusing on REEs have only recently gained attention due to their technological importance and growing environmental implications (Brito, Malvar et al., 2018; Brito, Mil-Homens et al., 2020; Mandal et al., 2019; Prasad & Ramanathan, 2008; Sappal et al., 2014). A comprehensive review study conducted by Khan et al. (2017) shed light on the speciation and bioavailability of REEs in soil, plant, and aquatic ecosystems, emphasizing their environmental impacts. The increased research interest in REEs in recent years is closely linked to their potential detrimental effects on living organisms, highlighting the importance of understanding their speciation, and bioavailability to evaluate associated health risks (M. Andrade et al., 2021; Henríquez-Hernández et al., 2017; Y. Ma et al., 2016; H. Zhang et al., 2010).

Studies conducted in mangroves along the Ganges River in India have revealed that plant activity does not substantially influence the retention of REEs in vegetated sediments (Mandal et al., 2019; Prasad & Ramanathan, 2008; Sappal et al., 2014). Instead, these studies suggest that the primary source of REEs in mangrove sediments is likely associated with the weathering of aluminosilicate materials from crustal sources, transported by fluvial processes. L. Costa, Johannesson, et al. (2021) have also observed that the presence of clay-silt sediment components plays a role in the accumulation of REEs by enhancing their adsorption onto mineral surfaces or through complexation with organic matter associated with these particles.

On the other hand, other studies have reported increased accumulation of REEs in mangrove-vegetated sediments from the Zhangjiang estuary in China (R. Zhang et al., 2013), Sepetiba Bay in Brazil (Silva-Filho et al., 2011), and Red Sea Mangroves in Saudi Arabia (Aljahdali & Alhassan, 2022). In these cases, the observed patterns were attributed to the variability of particle nature and the influence of anthropogenic inputs rather than the direct impact of plant activity.

A contrasting accumulation pattern was observed in the Jaguaripe estuary in Brazil (de Freitas et al., 2021), where mangrove-vegetated sediments exhibited lower REE content compared to adjacent estuarine sediments. This difference was also attributed to the characteristics of the sediment particles (grain size, organic matter and carbonate contents). The authors further investigated the depth profile variability of these elements in mangrove-vegetated sediments and found that the distribution of REEs is primarily controlled by post-depositional early diagenesis processes, mainly precipitation of Fe and Mn oxide/oxyhydroxides. In sites where redox-sensitive Fe and Mn showed minor variability with depth, substantial REE accumulation is not expected.

Sappal et al. (2014) proposed that fractionation of REEs in mangrove sediments is controlled by alkaline and reducing conditions, which lead to the removal of MREEs and LREEs through processes such as adsorption and precipitation onto Fe/Mn oxides/oxyhydroxides. Changes in ionic strength and REE-particle interactions also contribute to the REE fractionation (de Freitas et al., 2021; Mandal et al., 2019; Prasad & Ramanathan, 2008).

The redox status of the sediments plays a substantial role in the fractionation of Ce (Sholkovitz et al., 1992). Because these elements are redox-sensitive, and the redox status of mangrove sediments may change seasonally due to root oxygen input and Fe/Mn and S cycles, data on Ce anomalies are highly variable. Differences in anomaly patterns between plant organs and their surrounding rhizosediments (sedimentary environment that surrounds the root system) indicate that redox-driven biological processes influence the fractionation of Ce within the plant (de Sena et al., 2022). Additionally, the bioavailable fraction of these elements in the sediment also affects the anomalies observed in plant tissues.

L. Costa, Johannesson, et al. (2021) emphasize that Ce anomalies are influenced by early diagenetic processes and bioturbation. In Patos Lagoon (Brazil), Ce anomalies increase at sediment depths where oxic conditions are facilitated by burrowing crabs and saltmarsh plants, which enhance oxygen penetration. At greater sediment depths, the suboxic environment leads to lower Ce anomalies due to the reduction of Mn(IV) and Ce(IV), which mobilizes Ce(III) into the pore waters, resulting in decreased Ce content in the particulate fraction (de Sena et al., 2022).

The bioavailability of REEs plays a critical role in their transfer from soil to plants and their subsequent bioaccumulation in different plant tissues (Khan et al., 2017). However, most studies have focused on terrestrial plants, primarily in the context of plant-soil interactions in agriculture. The bioaccumulation of REEs depends on the availability of soluble and exchangeable fractions, which is influenced by various physicochemical environmental conditions such as ionic strength, dissolved organic carbon, total organic carbon, pH, redox status, cation exchange capacity, particle nature, and metal speciation (Arciszewska et al., 2022; Brito et al., 2021; Macmillan et al., 2019; Tyler, 2004; Weltje et al., 2004). These conditions exhibit wide variability in saltmarshes, seagrasses, and mangroves (de Sena et al., 2022).

Mandal et al. (2019) demonstrated that mangrove plants exhibit higher uptake of REE in belowground parts compared to aboveground plant tissues, although the total concentration of REE in the plants is lower than in the rhizosediment. The bioaccumulation and translocation factors show species-specific variability, indicating different partitioning of REEs and varying levels of efficiency in mangrove uptake (Alhassan & Aljahdali, 2021; Aljahdali & Alhassan, 2022; Mandal et al., 2019).

De Sena et al. (2022) conducted a study on seagrass meadows in Todos os Santos Bay (Brazil) to investigate the impact of environmental conditions that is, the proximity of reefs, mangroves, and sandy beaches, on sedimentary REE distribution. Similar to findings in mangroves, the retention of REEs in vegetated sediment is primarily influenced by particle nature and environmental settings. Seagrass roots were found to accumulate higher levels of REE compared to aboveground plant organs, although the overall accumulation was lower than in the sediment (de Sena et al., 2022; Komar et al., 2014). Interestingly, de Sena et al. (2022) noted that the low accumulation of REE in seagrass *Halodule wrightii*, along with limited translocation to aboveground plant parts, suggests a relatively low phytoaccumulation potential. In contrast, a different pattern was observed in *Cymodocea nodosa* in Makirina Bay (Croatia), with a translocation factor greater than 1, indicating the upward transfer of REEs through sediment-to-rhizome and/or water-to-leaf/epiphyte pathways (Komar et al., 2014). This suggests a preferential retention of REEs within the photosynthetic tissues of seagrass rather than in belowground plant parts. This could also be the result of the direct sorption from seawater (Zoll & Schijf, 2012). Notably, the uptake of REE by plants results in fractionation, with a preferential accumulation of HREE (de Sena et al., 2022). Organic ligands such as citric acid may play an important role in the transport of REEs in the xylem, leading to the enrichment of HREEs in aerial plant parts (Yuan et al., 2017).

Saltmarshes, colonized by halophyte plants, present increased sediment-root interaction compared with mangroves and seagrasses. In a study conducted by Brito, Prego et al. (2018) in the Rosário's saltmarsh in the Tagus estuary (southwest Europe), higher concentrations of REE were found in sediments colonized by *Sarcocornia fruticosa* and *Spartina maritima* compared to non-colonized sediments. This suggests that these plants may contribute to the enrichment of REEs in rhizosediments. The authors also observed higher REE concentrations in the roots compared with the aboveground parts of the plants, but no evidence of REE translocation within the plants. Additionally, distinct fractionation patterns were observed in the aboveground plant parts, with a clear enrichment of LREE relative to HREE, as well as an enrichment of MREE relative to LREE and HREE. A similar pattern was observed in another halophyte species, *Halimione portulacoides*, suggesting limited translocation of REEs to the upper organs or low retention of these elements in stems and leaves (Brito, Mil-Homens et al., 2020). In the marsh area, the authors identified specific layers of REE accumulation in the roots of *H. portulacoides*,

particularly for Y and MREE, indicating scavenging and accumulation in belowground organs, depending on the bioavailability rather than the total concentrations. Although salt marshes along with other vegetated coastal ecosystems are generally considered sinks for metals, including REEs, they can also act as a source of these elements (Caçador et al., 2009). This occurs through the uptake of metals from sediments by roots, translocation to the aboveground parts of plants, and subsequent return to the soil following senescence and the fall of aerial plant parts. Caçador et al. (2009) found that a sizeable fraction of metal-containing detritus is exported from the marsh, releasing substantial amounts of Zn, Cu, Co, and Cd (68, 8.2, 13 and 0.4 kg, respectively) per growing season. Although REEs exhibited low translocation factors from roots to aerial plant parts, further investigation is needed to evaluate the significance of this process in the REE cycle within estuaries and bays containing vegetated coastal ecosystems.

In summary, research has revealed various trends in REE accumulation within coastal vegetated ecosystems, influenced by factors such as sediment composition, environmental conditions, and human activities. The availability of REEs in sediments significantly impacts their uptake by plants, with studies highlighting species-specific differences in uptake and distribution among mangroves, saltmarshes, and seagrasses. Despite advancements, this field of study remains relatively novel, prompting further exploration into the role of vegetated coastal environments in the REE cycle and their potential as indicators for biogeochemical processes. Several hypotheses concerning REE dynamics within plant-soil systems require further investigation, along with the largely unexplored potential of REEs as tracers for both natural and anthropogenic processes.

### 2.3. Marine Sediments and Pore Water

The first dedicated investigation into marine pore water REE was conducted by Elderfield and Sholkovitz (1987) in 15 m deep water of Buzzard's Bay, MA, USA. Several studies followed this trend, all focusing on shallow waters (<300 m) (German & Elderfield, 1989; Sholkovitz et al., 1989, 1992). These studies alluded to the strong geochemical cycling of the REEs in the uppermost sediments. However, it was only more recent technological advances, in both sampling and analytical tools, that have enabled scientists to investigate REE behavior in open ocean sediments (Haley et al., 2004). As such, the potential importance of the sediment-water interface was not fully recognized until documentation of Nd isotopic alteration in bottom water near the sea floor (Lacan & Jeandel, 2004). Discovery of these deep water column isotopic anomalies offered an alternative, benthic explanation for the "Nd Paradox" (Goldstein & Hemming, 2003; Siddall et al., 2008); that is, an explanation that was not directly a function of water column processes (Lacan & Jeandel, 2005). While interest in these benthic processes is increasing, to date only <500 data exist for the REEs in pore water, a smaller subset of these having co-analyzed the sediment (for leachable phases and for the total sediment digest), and only a very small number of Nd isotope analyses of pore water (<30). About half of these pore water REE data are from samples >300 m deep in the oceans. A compilation of these data (Abbott, Haley, & McManus, 2015; Abbott, Haley, McManus & Reimers, 2015; Bayon et al., 2011; Deng et al., 2022; Deng et al., 2017; Elderfield & Sholkovitz, 1987; German & Elderfield, 1989; Haley et al., 2004; Patton et al., 2021; Sholkovitz et al., 1989; Sholkovitz et al., 1992) is tabulated in Supporting Information (Table S1).

Given the potential range in geochemical settings and the relative scarcity of pore water studies, much remains to be understood about the mechanisms involved in REE cycling in upper marine sediments. However, four overarching observations can be made with the data currently available. First, concentrations of REE in pore water in the upper sediments appear to be always elevated over bottom water (typically the maximum concentration in the water column). The implication of elevated pore water concentrations is that there is a ubiquitous benthic flux of REEs to the oceans. However, there are only a few attempts to estimate this flux (Abbott et al., 2019; Deng et al., 2017). Although much more data are required to make accurate global budgetary assessments, these order-of-magnitude estimates indicate that the benthic flux far exceeds surface ocean-sourced fluxes (such as rivers and dust). Moreover, it appears on par with the "missing flux" required to reconcile "Nd Paradox" (Abbott et al., 2019; Arsouze et al., 2007; Deng et al., 2017; Haley et al., 2017; Tachikawa et al., 2003). Estimates of SGD fluxes surpass these estimates, although both are benthic sources of REEs (Johannesson et al., 2011). Thus, there is good evidence to suggest that the benthic flux occurring within SGD, along the margins or at the bottom of the abyss is a critical, if not dominant, flux term in the global marine budget of REEs.

The second overarching observation is that whereas pore water supports a benthic source of REE to the ocean, the sediments remain the predominant sink for REE in the environment. Solid (e.g., biogenic fluorapatites, apatites,



phosphates, metal oxides minerals) and semi-solid phases (metal oxides, POM) are enriched in REE either through incorporation into the crystal lattice or via surface adsorption (e.g., Bayon et al., 2004; Bayon et al., 2011; Byrne & Sholkovitz, 1996; Du et al., 2022; Klinkhammer, 1980; Martin & Haley, 2000; Piper, 1974; Quadros et al., 2019; Schijf & Byrne, 2021; Schijf et al., 2015; Shaw & Wasserburg, 1985). Thus, the sediments act as a (dissolved) source and (particulate) sink of marine REEs, somewhat analogous to a capacitor (Haley et al., 2017). The largest sinks of REE appear to be Mn-oxides due to the ubiquity of this phase, and post-depositional phosphates (especially biogenic) due to their extreme REE enrichment (Abbott et al., 2016; Du et al., 2022; Takahashi et al., 2015; Toyoda & Tokonami, 1990). Whereas the latter is ostensibly a fairly inert sink term (although Du et al., 2022 indicate this may be otherwise), the former is certainly prone to changes in environmental redox state. That is, reduction of Mn-oxides that occurs in marine sediments can lead to release/cycling of REE (e.g., Froelich et al., 1979).

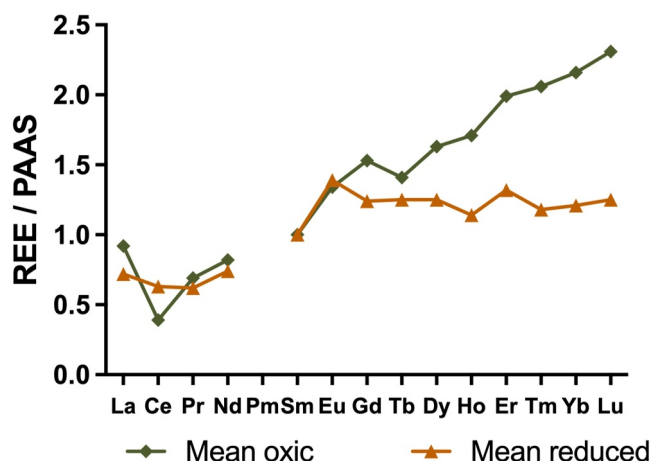
The fact that REEs are tightly coupled to Mn cycling appears to be a third generality of sedimentary REE geochemistry (Takahashi et al., 2015). Because Mn undergoes dynamic redox cycling between oxic and anoxic environments, the REEs also tend to show dynamic behavior in these sediments. In addition, the REEs have intricate complexation and readsorption behavior, which seems to make the association with Mn redox cycling unclear (Abbott et al., 2016; Du et al., 2022).

A fourth overarching observation is that pore water REEs also reflect input delivered by particulate organic matter (POM), but the details are more ambiguous. There is both laboratory and field evidence for strong association of REE with organic matter (OM) (Bau, 1996; Byrne & Kim, 1990; de Baar et al., 1988; Haley et al., 2004; Koeppenkastrop & De Carlo, 1992; Schijf et al., 1995; Sholkovitz, 1992; Stanley & Byrne, 1990; Tachikawa, Jeandel, Vangriesheim, & Dupré, 1999). Generally, the data all indicate that POM carries a LREE-enriched pattern (normalized to PAAS), whereas dissolved organic carbon (DOC) tends to complex and keep the HREE in solution. Unfortunately, there are very few direct analyses of REE in POM (Byrne & Kim, 1990; Davranche et al., 2005, 2011; Freslon et al., 2014; Pourret & Tuduri, 2017; Stanley & Byrne, 1990; Tachikawa, Jeandel, Vangriesheim, & Dupré, 1999). Furthermore, like Mn in the sediments, the tendency of REE to adsorb to surfaces (particularly OM surfaces), while the POM itself is undergoing remineralization, makes the relationship between POM and REE observationally abstruse. Sedimentary-based observations further suggest that Mn-oxides and POM are the predominant scavenging agents of REEs in the water column.

In addition to the four generalities mentioned above, marine sediment REEs exhibit distinct behaviors in oxic and anoxic conditions, although the mechanisms underlying each are still not fully understood. The inherent complexity arises from the kinetics of sedimentary processes, which are influenced by the temporal variability of inputs and the timescales of the chemical processes involved. In general, the REEs in oxic pore water are only moderately elevated over bottom water (Haley et al., 2004), with differences between the two most likely arising from changes in carbonate chemistry, and the resulting impact on dissolved REEs. The shale-normalized REE pattern of oxic pore water (Figure 6) is similar to the water column but commonly more pronounced (e.g., greater HREE/LREE; Haley et al., 2004). The amplification of the pattern could result from sedimentary processes mirroring those observed in the water column but compressed within the upper pore water. For instance, the organic complexing agents of the HREE could be more concentrated in the pore water compared to the water column.

In reducing pore water, dissolved REE abundances are generally far greater than in seawater, presumably reflecting an in situ input from metal oxides (Mn-oxides more likely than Fe-oxides) that are being reduced (as described above). The REE pattern of reducing pore water has a characteristic MREE enrichment when normalized to shale (Figure 6), which mirrors that of solid phase Mn-Fe oxides and some phosphates. However, there is nuance to these REE patterns beyond simple enrichment in MREE, which is likely crucial for understanding the ongoing processes. The cause for MREE enrichment in Mn-oxides is as yet uncertain; there is no evincing reason why the MREE would be relatively more incorporated over other REEs (Auer et al., 2017; Byrne & Sholkovitz, 1996; Hannigan & Sholkovitz, 2001; Koeppenkastrop & De Carlo, 1992; Lumiste et al., 2019; Reynard et al., 1999). It is possible that the MREE enrichment stems from relatively less available LREE (already adsorbed onto particles) and HREE (complexed) (Haley et al., 2021).

Cerium in pore water appears straightforward but is likely to be otherwise. There is clearly an Eh threshold that is reached whereby Ce(IV) is reduced to Ce(III), and [Ce] then acts like any other LREE in pore water (Haley et al., 2004). This can best be seen in reducing sediment cores, where the Ce-anomaly reaches a value of  $\sim 1$ .



**Figure 6.** Mean shale-normalized REE pattern of oxic (Abbott, Haley, McManus et al., 2015; Bayon et al., 2011; Deng et al., 2017, 2022; Haley et al., 2004) and reduced pore waters (Abbott, Haley, McManus et al., 2015; Deng et al., 2022; Elderfield & Sholkovitz, 1987; German & Elderfield, 1989; Himmler et al., 2013; J. Kim et al., 2012; Patton et al., 2021; Sholkovitz et al., 1989).

However, in many reducing pore waters, and overlapping oxic pore waters, the Ce-anomaly varies to values  $<0.2$ . Cerium concentration appears to be positively correlated to the Ce-anomaly in these oxic and sub-oxic pore waters, which implies that the relative release of solid Ce(IV) phases into pore water is not a true threshold, but a more complex interaction of solid phase Ce (IV), and reduced [Ce(III)] that is reacting and complexing like the other strictly trivalent LREE in solution. This complexity is consistent with observations of microbial mediation (Moffett, 1990) and/or an active role of organic ligands in Ce redox cycling (Kraemer & Bau, 2022). Moreover, as with all relational parameterizations, the Ce-anomaly is a function of its neighboring REE. The geochemical transformations of other LREE will cause the Ce-anomaly to vary even with static [Ce].

Use of neodymium isotopes in pore water offers a means to better determine the mechanisms involved in the source and sink functions of REEs in marine sediments. To date, there are very few observations ( $n \sim 30$ ) on the Nd isotopic composition of pore waters, largely due to the analytical hurdles associated with making these measurements. Pacific margin and slope pore water  $\epsilon_{Nd}$  appear to differ from the local bottom water, implying that there is a sedimentary source of “new” REEs in pore water (beyond that which is derived from the water column) (Abbott, Haley, McManus et al., 2015; Du et al., 2022). Mineral dissolution and secondary precipitation have been

observed in low-temperature settings on relatively short timescales (R. L. Andrade et al., 2020; Du et al., 2022; Jeandel & Oelkers, 2015; Lacan & Jeandel, 2005; Rousseau et al., 2015; Wilson et al., 2012, 2013). Thus, an immediate suggestion is that dissolution of the more reactive volcanic minerals drives the source of this “new” REE component, which is consistent with the more radiogenic  $\epsilon_{Nd}$  of the available data (Abbott et al., 2016; Abbott, Haley, McManus et al., 2015). The North Atlantic, however, shows evidence for the input of less-radiogenic benthic Nd (Du et al., 2022). How extensive this “new” REE source is and what it consists of are active questions that will have important implications for interpretations of both modern and past ocean REE and  $\epsilon_{Nd}$  compositions.

Deep sediment ( $>1$  m) pore water REE data are few, but indicate that REEs continue to react/fractionate during late stage diagenesis, at the sulfate:sulfide and methane fronts for instance (J. H. Kim et al., 2016). The dissolved REE will certainly reflect concomitant changes in the solid phase REE, which in turn may be preserved in sedimentary rock records and thus used as tools to understand depositional histories. Curiously, no pore water has as yet been found showing a relative MREE depletion (normalized to shale), one that might indicate loss to solid phases.

There are clearly many outstanding questions regarding marine sediment REEs, even fundamental questions such as: what are the relative roles of Mn-Oxides and phosphates—perhaps barites as well (Guichard et al., 1979; Haley & Klinkhammer, 2003; Martin et al., 1995)—as either sink or source terms to the ocean? What is the source of “new” REEs observed in sedimentary pore water? Is water column scavenging of REEs reversible or irreversible? Further emerging questions have yet to be properly posed, such as the possible effects of low-temperature recrystallization of minerals on the REE (especially that of the transition of the Mn-oxides birnessite to todorokite) (Atkins et al., 2014, 2016). Resolving these processes will also help us better understand the alteration of original signals to enable the use of REEs as tracers of past oceans (Bayon et al., 2004; Cao et al., 2022; Elderfield & Sholkovitz, 1987; Osborne et al., 2017; Palmer & Elderfield, 1986).

In summary, the sediment-water interface is a dynamic exchange interface for REEs. More than a simple sink, marine sediments seem to act also as a source for recycled water column REEs and a source of “new” REEs to the oceans. The magnitude of the source from all sediments appears to be greater than other estimates for terrestrial REE inputs and is especially significant in reducing sediments. The mechanisms for the recycling of water-column-scavenged and the generation of “new” REEs in marine sediments are still uncertain but appear in part to have strong ties to Mn-oxide redox cycling and POM remineralization. Improving our understanding of marine sediment REEs will help better define the budget of REEs in the ocean, likely helping to resolve the “Nd paradox” and provide better constraints on interpretations of modern and past marine REE and  $\epsilon_{Nd}$  data, as well as

informing us on the economic/societal potential of deep sea sediment-hosted REEs (Hein et al., 2020; Ijiri et al., 2018; Kato et al., 2011; Ohta et al., 2016; Takaya et al., 2018).

#### 2.4. Ocean

REE distributions in the ocean result from inputs from various sources previously detailed (i.e., rivers, SGD, sediment remobilization at the margins and bottom of the ocean, atmospheric deposits, and hydrothermal sources), advection by water masses and transformations in the water column (i.e., internal cycle). The processes influencing the internal cycle of REEs in the ocean encompass exchanges between dissolved and particulate phases: absorption, adsorption co-precipitation with authigenic minerals, desorption, remineralization, and particle dissolution. As particles represent the only oceanic sink for chemical elements, it is essential to identify and quantify these processes to estimate the oceanic mass balance of not only REE, but of all elements.

In the ocean, absorption occurs when REEs are incorporated into particles during their formation, particularly during primary production. There are two proposed pathways for REE incorporation: one involving methanotrophic bacteria and the other in diatom frustules. Methanotrophs can use REEs to replace calcium for catalyzing methane transformation (Keltjens et al., 2014), resulting in REE depletion in surface waters, which has a more pronounced effect on LREE (Bayon, Lemaitre, et al., 2020; Meyer et al., 2021; Shiller et al., 2017). Regarding frustules, Akagi et al. (2011) and Lagarde et al. (2020) have observed a HREE enrichment in comparison to LREE in particles that are significantly enriched in siliceous material. Akagi et al. (2011) made this observation with the siliceous fraction of settling particles in the Bering Sea and North Pacific Ocean corrected for the dominant terrigenous fraction, whereas Lagarde et al. (2020) conducted similar analysis on total particles in the Irminger and Labrador Seas during a declining diatom bloom. Akagi (2013) suggested a preferential incorporation of HREE driven by the fact that REE- $\text{H}_3\text{SiO}_4$  complexes are stronger for HREE than LREE. This calculation is based on formation constants established by Thakur et al. (2007) and Jensen and Choppin (1996), which have been significantly reassessed at a lower level by Soli and Byrne (2017) and Patten and Byrne (2017). Thus, the proportion of REE- $\text{H}_3\text{SiO}_4$  complexes established by Akagi (2013) appears to be greatly overestimated. To date, the connection between REEs and silica remains unclear, and a subject of debate.

Adsorption can occur on various constituents, including organic matter (Byrne & Kim, 1990; Zoll & Schijf, 2012), calcium carbonate (Palmer, 1985), opal, and Fe-Mn oxides/oxyhydroxides (Bau & Koschinsky, 2009; Ohta & Kawabe, 2001; Palmer & Elderfield, 1986). Even though Fe-Mn oxides/oxyhydroxides are recognized as major players in REE scavenging (Bau, 1999; Bau et al., 1996; Palmer & Elderfield, 1986; Schijf et al., 2015; Tachikawa, Jeandel, Vangriesheim, & Dupré, 1999), their role in the fractionation of REEs is not yet clearly established. There is evidence of a preferential adsorption of LREE by Fe hydroxides (Bau, 1999; Koeppenkaströp & De Carlo, 1993; Kuss et al., 2001; Schijf & Marshall, 2011) and by Mn oxides, which correlates with Particulate Organic Carbon (POC) concentrations and may result from bacterial activity (Kuss et al., 2001; Ohnuki et al., 2008). Conversely, Ohta and Kawabe (2001) found significant preferential adsorption of LREE on Mn oxides, which was not observed for Fe hydroxides in laboratory experiments. Among the REEs, Ce exhibits distinct behavior due to its additional oxidation state. In the ocean, its redox cycle is strongly linked to the Mn cycle (Bau & Dulski, 1996b; Elderfield, 1988; Moffett, 1990, 1994). Cerium oxidation can occur through abiotic processes, catalyzed by manganese oxides (Bau, 1999; Byrne & Kim, 1990; Koeppenkaströp & De Carlo, 1992) or through biotic processes, where microbial activity catalyzes it at the surface of particles (Moffett, 1990, 1994). The resulting Ce(IV) is sparingly soluble, leading to a Ce enrichment in particles compared to other REEs and a Ce depletion in seawater (Elderfield, 1988; Tachikawa, Jeandel, Vangriesheim, & Dupré, 1999). The role of Fe hydroxides in Ce scavenging is less clear. Bau and Koschinsky (2009) observed pronounced scavenging of Ce by both  $\text{MnO}_2$  and  $\text{Fe}(\text{OH})_3$  in ferromanganese crusts. However, experiments involving the addition of REEs during Mn oxide and Fe hydroxide precipitation showed little (Davranche et al., 2004) or no evidence of preferential Ce scavenging by Fe hydroxides (De Carlo et al., 1997; Koeppenkaströp & De Carlo, 1992; Ohta & Kawabe, 2001; Quinn et al., 2006; Schijf & Marshall, 2011).

Organic matter displays slightly negatively charged sites that can adsorb REEs. Adsorption on plants has been reported in several studies (M. Costa et al., 2020; de Sena et al., 2022; Pinto et al., 2020; Ramasamy et al., 2019; Santos et al., 2023), revealing a preferential LREE adsorption. Additionally, preferential HREE adsorption has been observed on bacterial cells (Moriwaki et al., 2013; Moriwaki & Yamamoto, 2013; Takahashi et al., 2005; Tsuruta, 2006). Haley et al. (2014) used the term “bio-active pool” to describe the influence of biological

processes observed in the distribution of dissolved REEs, which is attributed to bacterial activity. Sutorius et al. (2022) demonstrated, by incubation experiment, that the development of phytoplanktonic and associated bacterial development significantly impacts REE distribution through sorption processes and complexation with organic matter, although this effect is only observed during bloom periods.

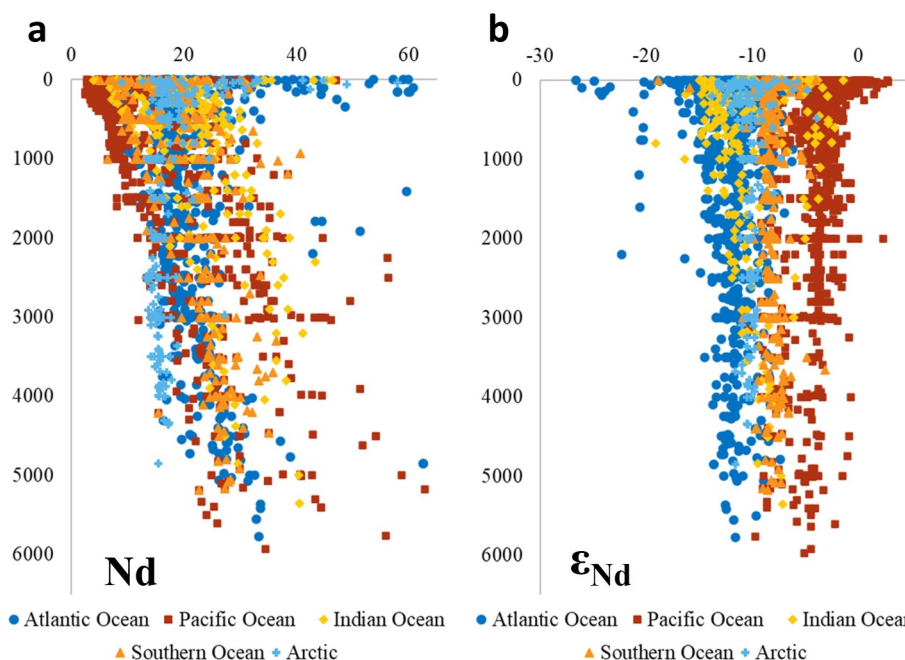
REEs can also be transferred to the particulate phase via co-precipitation with authigenic minerals such as rhabdophane (Pearce et al., 2013). Besides, there is also the possibility of co-precipitation of Ce with Mn oxides with different kinetics (Moffett, 1990, 1994).

The processes responsible for transferring REE from the particulate to the dissolved phase include: (a) desorption from particles (R. L. Andrade et al., 2020; Elderfield, 1988; Hara et al., 2009; Nozaki & Alibo, 2003; Sholkovitz et al., 1994), resulting in the enrichment of LREE in the dissolved phase due to their preferential adsorption; (b) particle disaggregation and dissolution (Byrne & Kim, 1990; Elderfield, 1988; Nozaki & Alibo, 2003; Sholkovitz et al., 1994; Stichel et al., 2015), and (c) remineralization of organic matter (Hara et al., 2009). As previously mentioned, the overall balance favors the preferential adsorption of LREE to HREE on particles, due to a competition between surface and solution complexation processes which each favor the HREE (Byrne & Kim, 1990; Elderfield, 1988; Elderfield et al., 1990; Elderfield & Greaves, 1982; Sholkovitz et al., 1994; Tachikawa, Jeandel, Vangriesheim, & Dupré, 1999), that are in higher proportion as free cations (Koeppenkastrup et al., 1991; Schijf et al., 2015; Sholkovitz et al., 1994). This scavenging effect is particularly pronounced for Ce as detailed above.

The particle-solution dynamics result in the nutrient-like distribution of REEs, which is strongly influenced by particle dynamics and explained by scavenging (Alibo & Nozaki, 1999; Garcia-Solsona et al., 2014; Haley et al., 2017; Nozaki & Alibo, 2003; Oka et al., 2021; R. Wang et al., 2021). There is currently active discussion on the nature of this scavenging, whether it is reversible or not (Haley et al., 2017; Siddall et al., 2008), a distinction that has a critical bearing on how REE and  $\epsilon_{Nd}$  are distributed in the oceans. For example, POM will remineralize in the water column, which has a different geochemical imprint on dissolved REE than Mn-oxide, which should not be prone to dissolution in oxygenated seawater. This results in a correlation between REE and nutrient distributions, observed with dissolved silica (de Baar et al., 1983; Elderfield, 1988; Garcia-Solsona et al., 2014; Hathorne et al., 2015; Pham et al., 2019; van de Flierdt et al., 2016; X. Y. Zheng et al., 2016), and to a lesser extent with phosphate and nitrate anions (de Baar et al., 2018; Garcia-Solsona et al., 2014; Hathorne et al., 2015). This correlation with silica is not observed everywhere in the ocean (de Baar et al., 2018; X. Y. Zheng et al., 2016), and suggests that REE and nutrient cycles are not coupled but are influenced by particle dynamics according to different processes, namely production and remineralization for nutrients, and reversible scavenging dependent on particle concentrations for REE (de Baar et al., 2018; Elderfield et al., 1988). At depth, distributions of regenerated nutrients and REEs released from particles would be correlated, mainly depending on the mixing of water masses (Osborne et al., 2017; van de Flierdt et al., 2016; X. Y. Zheng et al., 2016). The better correlation with silica compared to other nutrients could be explained by its better preservation in particles (de Baar et al., 2018), phosphate and nitrate remineralization being faster than REE enrichment by reversible scavenging. So far, the impact of phytoplankton and bacteria on the REE cycle remains unclear at a global scale, and the mechanisms behind it are far from being understood.

In addition to reversible scavenging and lithogenic/benthic inputs, the distributions of REEs depend on circulation, making them valuable tracers for these processes (de Baar et al., 2018; X. Y. Zheng et al., 2016). While REEs are suitable tracers for dissolved-particle exchanges, their optimal utilization requires either analyzing them in both phases or extracting the non-conservative fraction of the dissolved signal (X. Y. Zheng et al., 2016) in addition to analyzing dissolved normalized patterns.

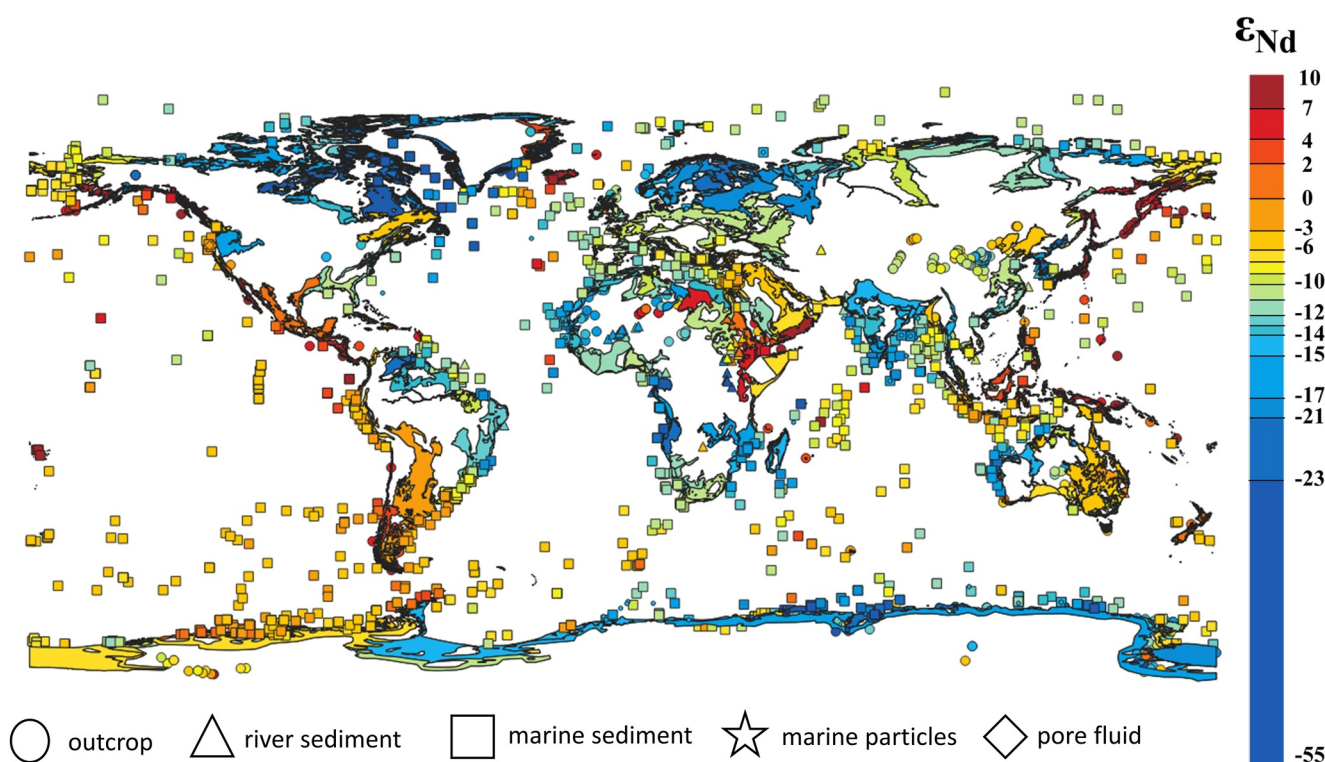
Among the REEs, Nd is studied more broadly through its isotopic composition ( $\epsilon_{Nd}$ ). Figure 7 shows a compilation of Nd concentration and IC in the global ocean (van de Flierdt et al., 2016). The clear variation in Nd isotopic composition between the 3 major ocean basins is not reflected in dissolved concentrations, which are more evenly distributed between the basins. This observation led to the “Nd Paradox”, missing term and “BE” concepts. Indeed, the recognition of the Nd paradox challenged the idea that rivers and atmospheric inputs are the main sources of REEs to the ocean, as these inputs are not sufficient to reconstruct the isotopic gradient observed between the Atlantic and the Pacific (Albarède et al., 1997; Jeandel & Peng, 1989; Tachikawa et al., 2003). Indeed, most large rivers and dust-reaching the Pacific have negative  $\epsilon_{Nd}$  values, approximately  $-10$ , poor in  $^{143}Nd$  (Goldstein et al., 1984; Goldstein & Jacobsen, 1988b; Jones et al., 1994; Nakai et al., 1993). It is important



**Figure 7.** Global ocean compilation of (a) dissolved Nd concentrations and (b) corresponding Nd isotopic composition ( $\epsilon\text{Nd}$ ). Data extracted from van de Flierdt et al. (2016), Filippova et al. (2017), Crocket et al. (2018), Paffrath et al. (2021) and Pham et al. (2022).

to note that changing the isotopic composition of water masses along their paths requires large inputs of elements, that is, doubling the variation in Nd concentration between the Atlantic and Pacific did not reflect the sheer number of inputs required to change the Nd isotopic composition. Researchers then began to suspect that ocean margins, whose significance was often mentioned but not quantified in terms of element mass balance calculations in the ocean, could play an important role in the observed variations of isotopic signatures (Jeandel et al., 1998; Lacan & Jeandel, 2001; Tachikawa et al., 2003). They believed that by using isotopes, they could quantify this role. Figure 8 presents a compilation of the margin Nd isotopic composition. A comparison with Figure 7 reveals that seawater tends to imprint the Nd isotopic composition of the surrounding continents, with the least and most radiogenic values in the Atlantic and in the Pacific, respectively (Garcia-Solsona et al., 2014; Grenier et al., 2013; Jendel et al., 1998; Lacan & Jeandel, 2001, 2005; Lambelet et al., 2016; Tachikawa et al., 2003; Wilson et al., 2012). In addition, REEs are about 6 orders of magnitude more concentrated in rocks ( $\mu\text{mol/kg}$ , Rudnick & Gao, 2003) than in seawater ( $\text{pmol/kg}$ , Figure 7). Thus, margin inputs are a good candidate to explain Nd isotopic composition variation along the thermohaline circulation. This was confirmed by measurements conducted in hydrographically invariant water masses that showed Nd isotopic composition variations together with rather constant Nd concentrations (Lacan & Jeandel, 2001, 2005; Tachikawa et al., 2003). Away from the margins and the sources they represent,  $\epsilon\text{Nd}$  behaves as a conservative tracer and its value is only influenced by the mixing of water masses (Jeandel, 1993; Piepgras & Wasserburg, 1982; von Blanckenburg, 1999). Consequently, it becomes a tracer of the mixing of water masses, with its evolution linked to the thermohaline circulation (Figure 7).

To explain this, one must pose that there is an input of Nd with a sufficiently different isotopic composition compared to seawater to significantly modify the latter. This input is likely to be quickly followed by the removal of Nd through adsorption onto marine particles. This process will decrease the Nd concentration in the water while retaining the isotopic signature resulting from the recent Nd addition. The element exchanges at the margins lead to the “Boundary Exchange” concept (Lacan & Jeandel, 2005), which involves the transfer of elements/isotopes across the interface separating seawater from sediments and rocks. Margin boundary processes include SGD inputs, partial dissolution of lithogenic sediments and benthic flux. This assumption was supported by observations of at least six continental margins (Lacan & Jeandel, 2005), then discussed and confirmed by more recent studies (Basak et al., 2015; Garcia-Solsona et al., 2014; Grenier et al., 2013; Lambelet et al., 2016; Rickli et al., 2014; Wilson et al., 2012). So far, the “Boundary Exchange” flux is not well constrained, and could



**Figure 8.**  $\epsilon_{Nd}$  in geological outcrops (dots), river sediment (triangles), marine sediment (squares), marine particles (stars), pore fluids (diamond), and interpolated continental  $\epsilon_{Nd}$  from the measured data. Data and interpolation method from Robinson et al. (2021).

contribute to offset the missing flux to balance the Nd oceanic budget, estimated at  $8 \times 10^9$  g/y (Tachikawa et al., 2003).

The Nd isotopic composition also appears to trace the influence of hydrothermal vents in mid-oceanic ridges, as indicated by changes in isotopic composition without changes in concentration (Chavagnac et al., 2018; Jeandel et al., 2013; Stichel et al., 2018). However, these results are still to be confirmed. Atmospheric dust also influences the isotopic composition of surface waters by dissolution (van de Flierdt et al., 2016). Their role has been demonstrated by modeling in the Mediterranean, where the atmospheric flux is high (Ayache et al., 2023).

In addition to field observations and mass balance calculations, the impact of “Boundary Exchange” on the global balance of Nd has been tested by coupling the assumed exchanges at margins into various general ocean circulation models (Gu et al., 2017; Rempfer et al., 2011; Siddall et al., 2008; Tachikawa et al., 2003) and regional models (Ayache et al., 2023). These models demonstrate that “Boundary Exchange” plays a dominant role in supplying Nd to the ocean, surpassing rivers and dust inputs by an order of magnitude ( $10^9$  vs.  $10^8$  g Nd.yr<sup>-1</sup>) (Rempfer et al., 2011; Tachikawa et al., 2003). Ayache et al. (2023) estimated that the marginal inputs represent ~80% of total Nd supply to the Mediterranean Sea. By dissolving only a small fraction (~0.1% to 3%, required by the model), substantial Nd inputs can be generated (Tachikawa et al., 2003). These models better simulate dissolved Nd concentrations when scavenging is reversible rather than irreversible, and also underscore the sensitivity of the models to the parametrized distribution of Nd between dissolved and particulate phases (Arsouze et al., 2009; Gu et al., 2017; Rempfer et al., 2011; Siddall et al., 2008).

“Boundary Exchange” processes are likely more intense in the first 500 m along the margins than in the abysses. It is probable that, due to the dynamics of more violent surface currents and internal tides, greater fluxes of particles together with faster and more efficient exchange processes occur in the upper 500 m than at depth (Barbot et al., 2022). Thus, the occurrence of clouds of suspended particles created by currents and undersea storms may also generate exchanges in deep water. If the processes responsible for generating “Boundary Exchange” (including their kinetics) are not explicitly described by field balances or models, the presumed dissolution of the lithogenic material implies that submarine alteration has occurred. Singh et al. (2012) demonstrated in the Bay of

Bengal that inputs of dissolved Nd released from sediments deposited by the river affect intermediate and deep waters. Similarly, the dissolution of labile phases of river-borne lithogenic sediments from the Mississippi River likely controls the Nd isotopic composition of the Gulf of Mexico (Adebayo et al., 2022). In the South China Sea, Y. Huang, Wu, and Hseu (2023) found that the seawater Nd isotopic composition was more effectively altered by pedogenic minerals from Chinese tropical soils, whereas the sediment from the Taiwan margin, consisting of fresh detrital material resulting from intense physical erosion of the Taiwan Island, had no significant impact. The relative influence of the different sediment and mineral-associated phases and their alteration still need to be understood.

In short, the study of REEs in the ocean reveals a complex interaction of various sources and processes influencing their distribution. From rivers to hydrothermal vents, these elements undergo absorption, desorption, co-precipitation, and remineralization, shaping their partitioning between dissolved and particulate phases. Conversely, this distribution can be traced back to the processes that determined it. The use of Nd isotopic composition ( $\epsilon\text{Nd}$ ) emerges as a crucial tracer, allowing the disentanglement of the relative importance of different sources of REE to the ocean: sediment deposited on ocean margins, hydrothermal activity, and atmospheric inputs. The concept of ‘Boundary Exchange’ underscores significant fluxes of REE across the seawater-sediment interface, with profound implications for oceanic budgets (not just REE) and circulation models. Both modeling efforts and empirical observations emphasize the dominant role of “Boundary Exchange” in supplying REEs to the ocean, with notable contributions from processes such as the dissolution of lithogenic material from rivers and submarine alteration, which significantly impact seawater Nd isotopic composition.

### 3. Anthropogenic Impacts on REE Distribution

Due to their remarkable catalytic, phosphorescent, and magnetic properties, REEs can significantly enhance a number of products and find applications in a wide range of fields, including industry, technology, agriculture, and medicine (Balaram, 2019; Gwenzi et al., 2018; Yuksekdag et al., 2022). Because of the increasing utilization of REEs over the past few decades, they are now considered emerging contaminants. Differentiating between contaminated and naturally enriched sites poses a substantial challenge (Kulaksiz & Bau, 2007; Nigro et al., 2018).

#### 3.1. Sources of Anthropogenic REE

Solid wastes, wastewaters, and air emissions from mining and mineral processing are substantial anthropogenic sources of REE (Gomes et al., 2022; Gwenzi et al., 2018; Ladonin, 2017; Lai et al., 2023; Lima & Ottosen, 2021; W. Liu et al., 2019; Massari & Ruberti, 2013; Schüler et al., 2011; Zapp et al., 2022). REE mining can also produce radioactive pollution, primarily from thorium and uranium (Kotelnikova et al., 2021; Massari & Ruberti, 2013). Another problem associated with the mining that is, acid mine drainage (AMD), known for releasing sulfuric acid, potentially toxic elements such as zinc (Zn), nickel (Ni), and copper (Cu), also increases the total content of REEs as well as the content of acid-soluble REEs (Ladonin, 2017). AMD-contaminated waters can have REE concentrations exceeding that of neutral freshwaters by 2–3 orders of magnitude and enrichment in MREEs (Gomes et al., 2022).

Certain industries have been applying REEs in their processes for decades when environmental contamination by REEs was still not a concern. For instance, sediments along the California coast have been contaminated with REEs since the 1960s due to petroleum-cracking catalysts and related by-products (Olmez et al., 1991). More recently, Kulaksiz and Bau (2013) also reported river water contamination with La and Sm due to industrial cracking catalyst production effluents. Fossil-fuel combustion and waste incineration have caused REE input to the soil, water, and air in the past several decades (Işıldar et al., 2018; Tan et al., 2015).

A recent study detailed the influence of historical steel-making processes on the REE composition and mobility in river sediment cores (Hissler et al., 2023). The disposal of industrial waste from steel production led to alterations in the shale normalized ratios of La/Lu and Y/Ho, as well as the enrichment of Eu, Yb, Sm, Ce, and Tm. Additionally, Hissler et al. (2023) demonstrated that REEs in contaminated sediments are more mobile compared to particles originating from soil erosion. Regions near steel plants can also be relatively enriched in Nd compared with other areas (Geagea et al., 2007; Hissler et al., 2008, 2016).

Recent applications of REEs in the technology industry, including superconductivity products, batteries, wind turbines, nuclear reactors, solar panels, permanent magnets, and cathode ray tubes, also contribute to contamination (L. Ma et al., 2019; L. Ma & Wang, 2023). For example, L. Ma & Wang (2023) identified Sm anomalies close to a permanent magnet industry. L. Ma et al. (2019) earlier found positive anomalies of Pr, Nd, Dy, and Ho in the same river, indicating the impact of REE recycling and other industrial activities in the area.

REEs possess exceptional properties useful for medical applications, including exhibiting potential antimicrobial activities comparable to copper (Cu) (Wakabayashi et al., 2016). Gadolinium is widely used as a contrast agent (Gd-CA) for magnetic resonance imaging (Bau & Dulski, 1996a; Raymond & Pierre, 2005; Telgmann et al., 2013). Gd-CAs, being stable and non-reactive, can pass through wastewater treatment and enter natural aquatic environments, leading to increased Gd concentrations in waters nearby densely populated areas with advanced healthcare systems, as shown in the pioneering work by Bau and Dulski (1996a). Temporal studies have reported 2 to 13-fold increases in anthropogenic Gd concentrations in the last decades in the Garonne River in France (Lerat-Hardy et al., 2019), and in coastal waters of California, USA, respectively (Hatje et al., 2016). Pedreira et al. (2018) estimated that biomedical applications in Brazil in 2016 discharged up to 2 kg Gd d<sup>-1</sup> into the Atlantic Ocean. Anthropogenic Gd has also been detected in lakes, groundwater, and tap water all around the world (e.g., Brünjes & Hofmann, 2020; Johannesson et al., 2017; Kulaksiz & Bau, 2011; Y. Liu et al., 2022; Merschel et al., 2015).

The REE-based fertilizers are a source of REE to soils (e.g., Bispo et al., 2021; Hu et al., 2006; F. B. V. Silva et al., 2019). However, data about the REE content in agricultural supplies worldwide are still limited, with most studies focusing on La, Ce, or REE mixtures and their effects on a few plant species (Tommasi et al., 2021). The amount of REE in fertilizers depends on the phosphorus content and source and the industrial process involved in the fertilizer manufacture (F. B. V. Silva et al., 2019; Turra et al., 2011). China, the largest REE-fertilizer consumer, employs between 50 and 100 million tons of REE oxides in agroecosystems, whereas Brazil, the world's fourth consumer of fertilizers, applies ~13,000 tons of REE annually to soils (F. B. V. Silva et al., 2019). Considering that the REE supplied by fertilizers is much more soluble and reactive than the regular soil pool (Tyler, 2004), this continuous practice may pose a risk to agricultural sustainability. Additionally, the production of phosphate fertilizers emits anthropogenic REEs into the environment, with phosphate plants contributing to substantial REE discharges (El Zrelli et al., 2021; Volokh et al., 1990). El Zrelli et al. (2021) estimated that a single phosphate fertilizer plant on the coast of Tunisia discharges annually up to 1,500 tons of REEs into the marine environment. The negative impacts of substantial REE inputs to soils extend beyond plants, as evidenced by correlated Sm anomalies ranging from 6 to 20 in the lakes of Wuhan due to agricultural activities (Y. Liu et al., 2022). Furthermore, positive Pr anomalies reported in estuarine sediments from Brazil were attributed to the manufacturing of monoammonium phosphate, a fertilizer product largely commercialized in Brazil (L. Costa, Mirlean. et al., 2021).

As the world continues to address the urgent need for decarbonization and transition to renewable energy sources, REEs have emerged as critical components in various technologies, such as electric vehicles, magnetic refrigeration, fluorescent lamps, nuclear reactors, and wind turbines (Evans et al., 2022; Pavel et al., 2017; Zhou et al., 2016). Although these alternatives offer substantial environmental benefits, their widespread adoption raises concerns about the potential pollution problems associated with the extraction, production, and disposal of REE products. In the scientific community, there are concerns about the future disposal of electric vehicle batteries and Nd-based permanent magnets when they reach the end of their life cycle. Although efforts are being made to develop efficient recycling systems (e.g., Binnemans et al., 2013, 2015; Nancharaiah et al., 2016), the sheer volume of these materials expected to reach the end of their life cycle in the coming decades poses a significant challenge. Improper disposal and dismissal of the entire lifecycle of these products could result in REEs and other metals leaching into the environment. Further research is still needed to understand the pathways and consequences of the anthropogenic inputs of REEs, as well as their large-scale and long-term implications for the environment and human health (F. Silva et al., 2019; Tariq et al., 2020; Tommasi et al., 2021).

### 3.2. Bioavailability, Bioaccumulation and Biomagnification

REE are found in organisms across various kingdoms, including Animalia, Plantae, Fungi, Protista, Bacteria, and Monera (Barrat et al., 2022; Brito et al., 2021; Chistoserdova, 2016; de Sena et al., 2022; Espejo et al., 2023; Liang & Shen, 2022; Marginson et al., 2023; Merschel & Bau, 2015; Ponnurangam et al., 2016; Santos et al., 2023;



Zocher et al., 2018). With the increase in anthropogenic activities, the input of REEs into the environment has risen, making it crucial to understand the processes that regulate their uptake by organisms and transfer across the food web. Additionally, it is crucial to understand the impact of their presence on biological systems, considering both individual and community levels.

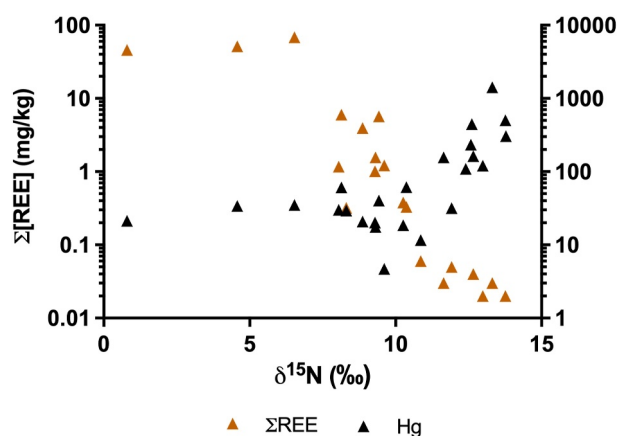
REE toxicity within the lanthanide group is not uniform. Some studies indicate that free REE toxic levels vary with atomic weight, and LREE promote higher toxicity than HREE, possibly due to the higher stability constants of the heavier elements (Blaise et al., 2018; Gonzalez et al., 2014; Lin et al., 2022). REE may cause various adverse effects, such as phytotoxicity, neurotoxicity, genotoxicity, cytotoxicity, endocrine disruption, and oxidative stress (Blaise et al., 2018; Y. Liu et al., 2019; Pagano et al., 2016; Xu et al., 2017). However, the ecological and human risks of REEs depend on their concentrations, chemical form, species sensitivity, age of the organism, route and duration of exposure, and interaction with other environmental factors (Badri et al., 2017; Gonzalez et al., 2014; C. Guo et al., 2020; Gwenzi et al., 2018; Souza et al., 2021; Tommasi et al., 2023; X. Zhang et al., 2022).

The toxicity of an element or its potential to have an adverse effect on organisms or ecosystems largely depends on its bioavailability. Bioavailability refers to the fraction of an element present in an environmental compartment that is available to cross an organism's cellular membrane (Luoma, 1983, 1989). After crossing the membrane, storage, transformation, degradation, and assimilation can occur within the organism. If a net accumulation of a contaminant in an organism from all possible intake routes, including water, air, and diet, occurs, the contaminant bioaccumulates in the organism (Chapman et al., 1996). In recent years, some studies have assessed the bioavailability and bioaccumulation of REEs, yielding variable results (Brito et al., 2021; Espejo et al., 2023; Orani et al., 2022; Paper et al., 2023; P. Zhao et al., 2022). Many factors influence the observed variability, and it is important to consider that each study compares the REE content in a specific group of organisms to a different environmental compartment, such as water or sediments/soils. Sediments, freshwater, and seawater, for instance, present very different REE concentrations and fractionation patterns, which influence the results and make direct comparisons between toxicological studies challenging.

Human exposure to REEs may also be a problem. Contamination of tap water by Gd contrast agents (Gd-CAs) has been observed in cities with highly developed healthcare systems, such as Berlin (Bau & Dulski, 1996a; Kulaksiz & Bau, 2011; Schmidt et al., 2019; Tepe et al., 2014), Düsseldorf and München (Schmidt et al., 2019), in Germany, London (UK) (Kulaksiz & Bau, 2011), and Prague (Czech Republic) (Möller et al., 2002). Gd contamination has also been observed in tap water-based popular carbonated soft drinks (Schmidt et al., 2019). Souza et al. (2021) identified high human bioaccessibility of Gd-CAs in tap water (i.e., >77% of Gd released in the gastrointestinal tract, therefore available for absorption), raising concerns about the potential toxicity of these contaminants to the human body when ingested above a certain threshold. On the other hand, Zocher et al. (2022) identified high REE bioaccumulation factors in duckweeds (i.e., three to five orders of magnitude), whereas Gd-CAs were considered unavailable. These contrasting results might exemplify how different biological systems deal with anthropogenic-derived REE species and how the route of intake may influence the bioavailability of these emerging contaminants.

REE bioavailability is specific to each element (Brito et al., 2021; de Sena et al., 2022). Furthermore, a mixture of REEs might show interactions that cause different impacts than individual REEs. Both antagonistic and additive effects have been reported for REE mixtures (Lachaux et al., 2022; E. Morel et al., 2021). Speciation, similar to other metals, plays a key role in REE bioavailability and toxicity. Arciszewska et al. (2022) indicated that bioavailability of dissolved species in aquatic systems decreases from free ions to inorganic complexes and to organic complexes. de Sena et al. (2022) also suggested that speciation of REEs in soils was a determining factor for the bioavailability and REE uptake by seagrasses.

Interactions between soil, plant roots, and microorganisms may increase REE bioavailability (Tyler, 2004; Zaharescu et al., 2017), which could become a concern, especially in areas fertilized with REE minerals or contaminated regions. X. Zhang et al. (2022) observed that REE affect bacterial communities causing reductions in biodiversity and abundance, along with the dominance of bacteria resistant to REE stress and capable of degrading the organic complexes formed by REE mining. Thus, bioavailable REEs exert an impact on the ecosystem and are reciprocally influenced by it.



**Figure 9.** Decrease in the concentration of the total REE and mercury along a trophic web, illustrated by the  $\delta^{15}\text{N}$ . The data indicate that REEs experienced trophic dilution, while Hg illustrates biomagnification. Adapted from Santos et al., 2023.

Some studies have shown species-specific and tissue-specific variations in the bioaccumulation of REEs, both in terms of total concentrations and fractionation patterns (MacMillan et al., 2017; Marginson et al., 2023; Santos et al., 2023; Squadrone et al., 2020). These studies suggest that detoxifying organs, such as the liver and kidneys, may serve as monitoring tissues, given their tendency to accumulate higher concentrations of REE compared to muscle tissue. Furthermore, observations in humans indicate that factors such as gender, age, alcohol consumption, and smoking habits can influence the concentrations and fractionation of REEs (Hao et al., 2015; Wei et al., 2013). These findings highlight the significance of considering ecological, environmental, physiological, and even social factors in the evaluation of REE transfer, accumulation, and distribution for risk assessments and food safety evaluations.

The transfer of REEs across the soil-plant system has been extensively studied, mainly because of its significant application in agriculture. Current findings indicate that the transfer of REEs from the environment to organisms is generally low, although some species (e.g., *Dicranopteris linearis*; H. Zheng et al., 2023) exhibit hyperaccumulation, making them potential candidates for REE mining and bioremediation of polluted sites (Chour et al., 2020; Liang & Shen, 2022; Orani et al., 2022; Paper et al., 2023).

The uptake of REEs from soils depends on various factors such as plant species as well as their growing conditions and the REE content in the substrate (Brioschi et al., 2013; Brito et al., 2021). Total concentrations of REE in soils typically do not serve as reliable predictors of concentrations in plants (Santos et al., 2023). However, uptake is positively correlated with soil acidity, soluble REE soil fractions, and organic matter content (Tyler, 2004). A study by Thomas et al. (2014) indicated that under more acidic conditions, the uptake and toxicity of REEs to terrestrial plants increased. In aquatic environments, REE bioaccumulation has been linked to lower pH levels and higher ratios of REE to dissolved organic carbon and free ion REE concentrations (Macmillan et al., 2019).

An important aspect that must be investigated when dealing with emerging contaminants like the REE is their trophic transfer capacity, which could lead to biomagnification or biodilution. However, this topic has been insufficiently studied thus far with regards to the REEs. The few available reports in the literature for aquatic and terrestrial ecosystems suggest not only a low potential for biomagnification of REEs but also a trend of biodilution across food webs (Amyot et al., 2017; MacMillan et al., 2017; Marginson et al., 2023; Santos et al., 2023; Squadrone et al., 2018). Biodilution is characterized by the decline in the concentration of REEs along the food web due to intake and elimination processes, resulting in a net loss of REEs from prey to predators, as illustrated in Figure 9. This behavior is opposite to that experienced by mercury (Hg) within the same trophic chain. From a human perspective, this finding is positive. However, given that REEs are emerging contaminants (Gwenzi et al., 2018; Hatje et al., 2014; Souza et al., 2021; Tepe et al., 2014), there are still knowledge gaps concerning their behavior and toxicity that need to be addressed to establish environmental and food safety thresholds for these elements.

### 3.3. REE and Anthropogenic Environmental Changes

The toxicity, bioavailability, bioaccumulation, reactivity, and fate of the REE are sensitive to environmental physico-chemical conditions. Co-occurrence of trace contaminants and other anthropogenic stressors such as climate change (CC) drivers (e.g., warming, altered precipitation patterns, deoxygenation, acidification, extreme events, changes in ocean circulation and mixing) can amplify the effects of contaminants on the ecosystem health, services, and functions (Hatje et al., 2022). These stressors may alter bioaccumulation and toxicity patterns, thereby influencing organism's responses (Boukadida et al., 2016; Leite et al., 2020, 2023) and potentially compromising food security.

Recent attention has been given to the effect of CC drivers on trace elements (Cabral et al., 2019; Gwynn et al., 2024; Hatje et al., 2022; Jin et al., 2021; Pan et al., 2023). However, studies specifically concerning the effects of CC drivers on REEs are scarce. Additionally, the impacts of temperature, pH, and salinity shifts on REE

geochemistry have received more attention than other drivers such as sea-level rise, acidification, deoxygenation, and extreme events. For example, an increase in temperature from 17 to 21°C has been observed to increase Nd accumulation in *Mytilus galloprovincialis*, possibly associated with a slight decrease in detoxification capacity (GSTs activity; Leite et al., 2023). A recent study involving the same species found that the interaction between Pr and elevated temperatures resulted in histopathological injuries, redox imbalance, and cellular damage (Leite et al., 2024). These findings align with the results observed for mussels exposed to Ce oxide nanoparticles and mercury at increased temperatures (Morosetti et al., 2020). However, the warmer temperatures did not cause more damage to mussel gills than Nd and temperature acting separately (Leite et al., 2023). On the other hand, Nd and temperature had a higher impact on mussel digestive tracts (Leite et al., 2023). The impact on organisms may not only depend on the emerging interactions between contaminants and CC drivers (e.g., temperature rise during a heat wave) but also on the exposure duration (Leite et al., 2020, 2023). Higher temperatures may facilitate the elimination of certain contaminants (Figueiredo et al., 2022; Maulvault et al., 2018). For example, La elimination by *Spisula solida* was more efficient under higher temperatures than under control conditions (Figueiredo et al., 2022).

Salinity, which can vary under changing precipitation, evaporation scenarios, or ice melting due to CC, is another important factor. Salinity influences metal speciation, metal bioavailability, and organism metabolism. Higher salinity has been shown to increase metal uptake in marine mussels due to a decrease in chloride complexation, leading to increased free metal ions (Campbell, 1995). Low salinity may also cause higher metabolism, favoring contaminant accumulation (Freitas et al., 2020). A recent study showed that higher metabolism of bivalves at salinity 20 enhanced the accumulation of La and was closely related to the organisms' biochemical performance (i.e., antioxidant activity and biotransformation defenses activation) and cellular damage (M. Andrade et al., 2021). The dual stress from increased salinity and La concentrations may overwhelm the defense mechanisms and this combination may also cause neurotoxicity (Andrade et al., 2021).

Climate-induced events, such as drying of tailing piles, drier soils, and lowering of the water table, may expose sulfidic minerals to oxic conditions, resulting in prolonged periods of baseflow with lower pH and higher solute concentrations (Rue & McKnight, 2021). In such conditions, REEs may be mobilized through primary weathering of sulfide and silicate minerals. Rue and McKnight (2021) showed that REE concentrations and fluxes increased with increasing air temperature over the past 30 years. This new contribution of REEs raises concerns for aquatic ecosystems and the quality of drinking water sources. However, no drinking water quality standards exist for REEs, and questions remain regarding exposure thresholds for impacts on aquatic life and human health.

Although there are significant knowledge gaps, it is expected that the CC drivers of concern for radionuclides (Gwynn et al., 2024) and toxic metals will impact REEs in similar ways. For instance, the surface pH of seawater will decrease by 0.1–0.4 units (Cooley et al., 2022) and will impact the speciation, bioavailability, and overall biogeochemical behavior of trace elements. Metals that form strong complexes with carbonates, phosphates, and silicates, such as REEs, will be strongly affected by changes in pH, resulting in an increase in their free ionic forms. The free form of REEs will increase by 15%–24% under more acidic conditions (Millero et al., 2009).

The interaction of REEs with CC and other anthropogenic drivers could lead to significant impacts at high biological levels. A better understanding of the emerging interactions between CC and REEs is crucial for predicting future changes across the land-ocean continuum. This comprehension will be instrumental in developing effective measures to protect ecosystems.

#### 4. Conclusions

There is substantial evidence supporting the significant contribution and usefulness of REEs as tracers or proxies in comprehending geochemical processes in both oceanic and terrestrial environments. Although the application of REEs to assess biological processes is still in its early stages, preliminary studies show promising potential. Additionally, REEs can function as micronutrients and contaminants.

Although the sources and sinks of these elements are relatively well understood, the REE mass balance in the ocean is not completely resolved; for instance, the impact of boundary exchange and inputs from SGD need more studies. Besides, it is essential to consider the potential impact of anthropogenic activities and global climate change. Such factors could significantly alter the concentrations, speciation, distribution patterns, and residence time of REEs in environmental compartments.

Moreover, there is a crucial need to investigate the potential health effects of anthropogenic REEs on ecosystems and human health. Therefore, investments aimed at improving our understanding of the life cycle of REEs, from mining and ore processing to the final disposition and recycling of REE products, should be encouraged. This becomes particularly relevant as society transitions to low-carbon energy, where REEs play a key role in electronics production.

In conclusion, further research and awareness are essential to effectively harness the benefits of REEs while mitigating any potential negative consequences. A comprehensive understanding of their behavior and impact is crucial for sustainable and responsible usage of these valuable elements in various sectors.

## Data Availability Statement

Data were not used or created for this research.

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## References

- Abbott, A. N. (2019). A benthic flux from calcareous sediments results in non-conservative neodymium behavior during lateral transport: A study from the Tasmanian Sea. *Geology*, *47*(4), 363–366. <https://doi.org/10.1130/G45904.1>
- Abbott, A. N., Haley, B. A., & McManus, J. (2015). Bottoms up: Sedimentary control of the deep North Pacific Ocean's  $\epsilon$ Nd signature. *Geology*, *43*(11), 1035–1038. <https://doi.org/10.1130/G37114.1>
- Abbott, A. N., Haley, B. A., & McManus, J. (2016). The impact of sedimentary coatings on the diagenetic Nd flux. *Earth and Planetary Science Letters*, *449*, 217–227. <https://doi.org/10.1016/j.epsl.2016.06.001>
- Abbott, A. N., Haley, B. A., McManus, J., & Reimers, C. E. (2015). The sedimentary flux of dissolved rare earth elements to the ocean. *Geochimica et Cosmochimica Acta*, *154*, 186–200. <https://doi.org/10.1016/j.gca.2015.01.010>
- Abbott, A. N., Lühr, S., & Trethewey, M. (2019). Are clay minerals the primary control on the oceanic rare earth element budget? *Frontiers in Marine Science*, *6*(AUG), 1–19. <https://doi.org/10.3389/fmars.2019.00504>
- Abdelnour, S. A., Abd El-Hack, M. E., Khafaga, A. F., Noreldin, A. E., Arif, M., Chaudhry, M. T., et al. (2019). Impacts of rare earth elements on animal health and production: Highlights of cerium and lanthanum. *Science of the Total Environment*, *672*, 1021–1032. <https://doi.org/10.1016/j.scitotenv.2019.02.270>
- Adebayo, S. B., Cui, M., Hong, T., Akintomide, O., Kelly, R. P., & Johannesson, K. H. (2020). Rare earth element cycling and reaction path modeling across the chemocline of the Pettaquamscutt River estuary, Rhode Island. *Geochimica et Cosmochimica Acta*, *284*, 21–42. <https://doi.org/10.1016/j.gca.2020.06.001>
- Adebayo, S. B., Cui, M., Hong, T., White, C. D., Johannesson, K. H., & Martin, E. E. (2018). Rare earth elements geochemistry and Nd isotopes in the Mississippi river and Gulf of Mexico mixing zone. *Frontiers in Marine Science*, *5*(May), 1–18. <https://doi.org/10.3389/fmars.2018.00166>
- Adebayo, S. B., Cui, M., Williams, T. J., Martin, E., & Johannesson, K. H. (2022). Evolution of rare earth element and  $\epsilon$ Nd compositions of Gulf of Mexico seawater during interaction with Mississippi River sediment. *Geochimica et Cosmochimica Acta*, *335*, 231–242. <https://doi.org/10.1016/j.gca.2022.08.024>
- Akagi, T. (2013). Rare earth element (REE)–silicic acid complexes in seawater to explain the incorporation of REEs in opal and the “leftover” REEs in surface water: New interpretation of dissolved REE distribution profiles. *Geochimica et Cosmochimica Acta*, *113*, 174–192. <https://doi.org/10.1016/j.gca.2013.03.014>
- Akagi, T., Fu, F., Hongo, Y., & Takahashi, K. (2011). Composition of rare earth elements in settling particles collected in the highly productive North Pacific Ocean and Bering Sea: Implications for siliceous-matter dissolution kinetics and formation of two REE-enriched phases. *Geochimica et Cosmochimica Acta*, *75*(17), 4857–4876. <https://doi.org/10.1016/j.gca.2011.06.001>
- Albarède, F., Goldstein, S. L., & Dautel, D. (1997). The neodymium isotopic composition of manganese nodules from the Southern and Indian oceans, the global oceanic neodymium budget, and their bearing on deep ocean circulation. *Geochimica et Cosmochimica Acta*, *61*(6), 1277–1291. [https://doi.org/10.1016/S0016-7037\(96\)00404-8](https://doi.org/10.1016/S0016-7037(96)00404-8)
- Alhassan, A. B., & Aljahlali, M. O. (2021). Fractionation and distribution of rare earth elements in marine sediment and bioavailability in avicennia marina in central red sea mangrove ecosystems. *Plants*, *10*(6), 1233. <https://doi.org/10.3390/plants10061233>
- Alibo, D. S., & Nozaki, Y. (1999). Rare earth elements in seawater: Particle association, shale-normalization, and Ce oxidation. *Geochimica et Cosmochimica Acta*, *63*(3/4), 363–372. [https://doi.org/10.1016/S0016-7037\(98\)00279-8](https://doi.org/10.1016/S0016-7037(98)00279-8)
- Alibo, D. S., & Nozaki, Y. (2004). Dissolved rare earth elements in the eastern Indian Ocean: Chemical tracers of the water masses. *Deep-Sea Research Part I Oceanographic Research Papers*, *51*(4), 559–576. <https://doi.org/10.1016/j.dsr.2003.11.004>
- Aljahlali, M. O., & Alhassan, A. B. (2022). Rare earth elements and bioavailability in northern and southern Central Red Sea Mangroves, Saudi Arabia. *Molecules*, *27*(14), 4335. <https://doi.org/10.3390/molecules27144335>
- Amyot, M., Clayden, M. G., Macmillan, G. A., Perron, T., & Arscott-Gauvin, A. (2017). Fate and trophic transfer of rare earth elements in temperate lake food webs. *Environmental Science and Technology*, *51*(11), 6009–6017. <https://doi.org/10.1021/acs.est.7b00739>
- Anderson, R. (2020). GEOTRACES: Accelerating research on the marine biogeochemical cycles of trace elements and their isotopes. *Annual Review of Marine Science*, *12*(1), 49–85. <https://doi.org/10.1146/annurev-marine-010318-095123>
- Anderson, R., Mawji, E., Cutter, G. A., Measures, C. I., & Jeandel, C. (2014). GEOTRACES: Changing the way we explore ocean chemistry. *Oceanography*, *27*(1), 50–61. <https://doi.org/10.5670/oceanog.2014.07>
- Andrade, M., Soares, A. M. V. M., Solé, M., Pereira, E., & Freitas, R. (2021). Salinity influences on the response of *Mytilus galloprovincialis* to the rare-earth element lanthanum. *Science of the Total Environment*, *794*, 148512. <https://doi.org/10.1016/j.scitotenv.2021.148512>
- Andrade, R. L., Hatje, V., Pedreira, R. M., Boening, P., & Pahnke, K. (2020). REE fractionation and human Gd footprint along the continuum between Paraguaçu River to coastal South Atlantic waters. *Chemical Geology*, *532*, 119303. <https://doi.org/10.1016/j.chemgeo.2019.119303>
- Arciszewska, Ż., Gama, S., Leśniewska, B., Malejko, J., Nalewajko-Sieliwoniuk, E., Zambrzycka-Szelewa, E., & Godlewska-Zyłkiewicz, B. (2022). The translocation pathways of rare earth elements from the environment to the food chain and their impact on human health. *Process Safety and Environmental Protection*, *168*, 205–223. <https://doi.org/10.1016/j.psep.2022.09.056>

- Arsouze, T., Dutay, J. C., Lacan, F., & Jeandel, C. (2007). Modeling the neodymium isotopic composition with a global ocean circulation model. *Chemical Geology*, 239(1–2), 165–177. <https://doi.org/10.1016/j.chemgeo.2006.12.006>
- Arsouze, T., Dutay, J.-C., Lacan, F., & Jeandel, C. (2009). Reconstructing the Nd oceanic cycle using a coupled dynamical – Biogeochemical model. *Biogeosciences Discussions*, 6(3), 5549–5588. <https://doi.org/10.5194/bgd-6-5549-2009>
- Atkins, A. L., Shaw, S., & Peacock, C. L. (2014). Nucleation and growth of todorokite from birnessite: Implications for trace-metal cycling in marine sediments. *Geochimica et Cosmochimica Acta*, 144, 109–125. <https://doi.org/10.1016/j.gca.2014.08.014>
- Atkins, A. L., Shaw, S., & Peacock, C. L. (2016). Release of Ni from birnessite during transformation of birnessite to todorokite: Implications for Ni cycling in marine sediments. *Geochimica et Cosmochimica Acta*, 189, 158–183. <https://doi.org/10.1016/j.gca.2016.06.007>
- Auer, G., Reuter, M., Hauzenberger, C. A., & Piller, W. E. (2017). The impact of transport processes on rare earth element patterns in marine authigenic and biogenic phosphates. *Geochimica et Cosmochimica Acta*, 203, 140–156. <https://doi.org/10.1016/j.gca.2017.01.001>
- Ayache, M., Dutay, J. C., Tachikawa, K., Arsouze, T., & Jeandel, C. (2023). Neodymium budget in the Mediterranean Sea: Evaluating the role of atmospheric dusts using a high-resolution dynamical-biogeochemical model. *Biogeosciences*, 20(1), 205–227. <https://doi.org/10.5194/bg-20-205-2023>
- Ayora, C., Macías, F., Torres, E., & Nieto, J. M. (2015). Rare earth elements in acid mine drainage. *XXXV Reunión de la Sociedad Española de Mineralogía; Sociedad Espanola de Mineralogía: Huelva, Spain*, 1–22.
- Babu, S. S., Venkata Ramana, R., Purnachandra Rao, V., Ram Mohan, M., Sawant, S., Satyasree, N., & Keshav Krishna, A. (2021). Rare earth elements of sediments in rivers and estuaries of the East Coast of India. *Current Science*, 120(3), 519. <https://doi.org/10.18520/cs/v120/i3/519-537>
- Badri, N., Florea, A., Mhamdi, M., Matei, H., Tekaya, W. H., Bâati, R., et al. (2017). Toxicological effects and ultrastructural changes induced by lanthanum and cerium in ovary and uterus of Wistar rats. *Journal of Trace Elements in Medicine & Biology*, 44(August), 349–355. <https://doi.org/10.1016/j.jtemb.2017.09.011>
- Balaram, V. (2019). Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*, 10(4), 1285–1303. <https://doi.org/10.1016/j.gsf.2018.12.005>
- Banfield, J. F., & Eggleton, R. A. (1989). Apatite replacement and rare earth mobilization, fractionation, and fixation during weathering. *Clays and Clay Minerals*, 37(2), 113–127. <https://doi.org/10.1346/CCMN.1989.0370202>
- Banks, D. A., Yardley, B. W. D., Campbell, A. R., & Jarvis, K. E. (1994). REE composition of an aqueous magmatic fluid: A fluid inclusion study from the Capitan Pluton, New Mexico, U.S.A. *Chemical Geology*, 113(3–4), 259–272. [https://doi.org/10.1016/0009-2541\(94\)90070-1](https://doi.org/10.1016/0009-2541(94)90070-1)
- Banner, J. L., Hanson, G. N., & Meyers, W. J. (1988). Rare earth element and Nd isotope variations in regionally extensive dolomites from the Burlington-Keokuk Formation (Mississippian): Implications for REE mobility during carbonate diagenesis. *Journal of Sedimentary Petrology*, 58, 415–432.
- Bao, S.-X., Zhou, H.-Y., Peng, X.-T., Ji, F.-W., & Yao, H.-Q. (2008). Geochemistry of REE and yttrium in hydrothermal fluids from the Endeavour segment, Juan de Fuca Ridge. *Geochemical Journal*, 42(4), 359–370. <https://doi.org/10.2343/geochemj.42.359>
- Barbot, S., Lagarde, M., Lyard, F., Marsaleix, P., Lherminier, P., & Jeandel, C. (2022). Internal tides responsible for lithogenic inputs along the Iberian continental slope. *Journal of Geophysical Research: Oceans*, 127(10). <https://doi.org/10.1029/2022JC018816>
- Barrat, J. A., Bayon, G., & Lalonde, S. (2023). Calculation of cerium and lanthanum anomalies in geological and environmental samples. *Chemical Geology*, 615, 121202. <https://doi.org/10.1016/j.chemgeo.2022.121202>
- Barrat, J. A., Boulègue, J., Tiercelin, J. J., & Lesourd, M. (2000). Strontium isotopes and rare-earth element geochemistry of hydrothermal carbonate deposits from Lake Tanganyika, east Africa. *Geochimica et Cosmochimica Acta*, 64(2), 287–298. [https://doi.org/10.1016/S0016-7037\(99\)00294-X](https://doi.org/10.1016/S0016-7037(99)00294-X)
- Barrat, J. A., Chauvaud, L., Olivier, F., Poitevin, P., Bayon, G., & Ben Salem, D. (2022). Rare earth elements and yttrium in suspension-feeding bivalves (dog cockle, *Glycymeris glycymeris* L.): Accumulation, vital effects and pollution. *Geochimica et Cosmochimica Acta*, 339, 12–21. <https://doi.org/10.1016/j.gca.2022.10.033>
- Basak, C., Pahnke, K., Frank, M., Lamy, F., & Gersonde, R. (2015). Neodymium isotopic characterization of Ross Sea Bottom Water and its advection through the southern South Pacific. *Earth and Planetary Science Letters*, 419, 211–221. <https://doi.org/10.1016/j.epsl.2015.03.011>
- Bau, M. (1996). Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology*, 123(3), 323–333. <https://doi.org/10.1007/s004100050159>
- Bau, M. (1999). Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta*, 63(1), 67–77. [https://doi.org/10.1016/S0016-7037\(99\)00014-9](https://doi.org/10.1016/S0016-7037(99)00014-9)
- Bau, M., Alexander, B., Chesley, J. T., Dulski, P., & Brantley, S. L. (2004). Mineral dissolution in the Cape Cod aquifer, Massachusetts, USA: I. Reaction stoichiometry and impact of accessory feldspar and glauconite on strontium isotopes, solute concentrations, and REY distribution. *Geochimica et Cosmochimica Acta*, 68(6), 1199–1216. <https://doi.org/10.1016/j.gca.2003.08.015>
- Bau, M., & Dulski, P. (1996a). Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth and Planetary Science Letters*, 143(1–4), 245–255. [https://doi.org/10.1016/0012-821X\(96\)00127-6](https://doi.org/10.1016/0012-821X(96)00127-6)
- Bau, M., & Dulski, P. (1996b). Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Research*, 79(1–2), 37–55. [https://doi.org/10.1016/0301-9268\(95\)00087-9](https://doi.org/10.1016/0301-9268(95)00087-9)
- Bau, M., & Dulski, P. (1999). Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: Implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater. *Chemical Geology*, 155(1–2), 77–90. [https://doi.org/10.1016/S0009-2541\(98\)00142-9](https://doi.org/10.1016/S0009-2541(98)00142-9)
- Bau, M., & Koschinsky, A. (2009). Oxidative scavenging of cerium on hydrous Fe oxide: Evidence from the distribution of rare earth elements and yttrium between Fe oxides and Mn oxides in hydrogenetic ferromanganese crusts. *Geochemical Journal*, 43(1), 37–47. <https://doi.org/10.2343/geochemj.1.0005>
- Bau, M., Koschinsky, A., Dulski, P., & Hein, J. R. (1996). Comparison of the partitioning behaviours of yttrium, rare earth elements, and titanium between hydrogenetic marine ferromanganese crusts and seawater. *Geochimica et Cosmochimica Acta*, 60(10), 1709–1725. [https://doi.org/10.1016/0016-7037\(96\)00063-4](https://doi.org/10.1016/0016-7037(96)00063-4)
- Bau, M., Schmidt, K., Pack, A., Bendel, V., & Kraemer, D. (2018). The European Shale: An improved data set for normalisation of rare earth element and yttrium concentrations in environmental and biological samples from Europe. *Applied Geochemistry*, 90(January), 142–149. <https://doi.org/10.1016/j.apgeochem.2018.01.008>
- Bayon, G., Birot, D., Ruffine, L., Caprais, J., Ponzevera, E., Bollinger, C., et al. (2011). Evidence for intense REE scavenging at cold seeps from the Niger Delta margin. *Earth and Planetary Science Letters*, 312(3–4), 443–452. <https://doi.org/10.1016/j.epsl.2011.10.008>
- Bayon, G., Douglas, G. B., Denton, G. J., Monin, L., & De Deckker, P. (2020). Preferential riverine export of fine volcanogenic particles to the southeast Australian margin. *Frontiers in Marine Science*, 7, 89. <https://doi.org/10.3389/fmars.2020.00089>

- Bayon, G., German, C. R., Burton, K. W., Nesbitt, R. W., & Rogers, N. (2004). Sedimentary Fe-Mn oxyhydroxides as paleoceanographic archives and the role of aeolian flux in regulating oceanic dissolved REE. *Earth and Planetary Science Letters*, 224(3–4), 477–492. <https://doi.org/10.1016/j.epsl.2004.05.033>
- Bayon, G., Lemaître, N., Barrat, J.-A., Wang, X., Feng, D., & Duperron, S. (2020). Microbial utilization of rare earth elements at cold seeps related to aerobic methane oxidation. *Chemical Geology*, 555, 119832. <https://doi.org/10.1016/j.chemgeo.2020.119832>
- Bayon, G., Toucanne, S., Skonieczny, C., André, L., Bermell, S., Cheron, S., et al. (2015). Rare earth elements and neodymium isotopes in world river sediments revisited. *Geochimica et Cosmochimica Acta*, 170, 17–38. <https://doi.org/10.1016/j.gca.2015.08.001>
- Beers, Y. (1957). *Introduction to the theory of error* (2nd ed.). Addison-Wesley Publishing Co.
- Bellefroid, E. J., Hood, A. V. S., Hoffman, P. F., Thomas, M. D., Reinhard, C. T., & Planavsky, N. (2018). Constraints on Paleoproterozoic atmospheric oxygen levels. *Proceedings of the National Academy of Sciences*, 115(32), 8104–8109. <https://doi.org/10.1073/pnas.1806216115>
- Berner, R. A. (1980). *Early diagenesis: A theoretical approach*. Princeton University Press.
- Biddau, R., Bensimon, M., Cidu, R., & Parriaux, A. (2009). Rare earth elements in groundwater from different Alpine aquifers. *Chemie der Erde*, 69(4), 327–339. <https://doi.org/10.1016/j.chemer.2009.05.002>
- Bigot, S., Treuil, M., Dumonceau, J., & Fromage, F. (1984). Couplage des équations de transfert de masse et des lois d'interactions solution-solide par l'utilisation des lanthanides comme traceurs — Approche expérimentale. *Journal of Hydrology*, 70(1–4), 133–148. [https://doi.org/10.1016/0022-1694\(84\)90118-5](https://doi.org/10.1016/0022-1694(84)90118-5)
- Binnemans, K., Jones, P. T., Blanpain, B., Van Gerven, T., & Pontikes, Y. (2015). Towards zero-waste valorisation of rare-earth-containing industrial process residues: A critical review. *Journal of Cleaner Production*, 99, 17–38. <https://doi.org/10.1016/j.jclepro.2015.02.089>
- Binnemans, K., Jones, P. T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., & Buchert, M. (2013). Recycling of rare earths: A critical review. *Journal of Cleaner Production*, 51, 1–22. <https://doi.org/10.1016/j.jclepro.2012.12.037>
- Bispo, F., Menezes, M., Fontana, A., Sarkis, J. S., Gonçalves, C., Carvalho, T., et al. (2021). Rare earth elements (REEs) geochemical patterns and contamination aspects in Brazilian benchmark soils. *Environmental Pollution*, 289, 11792. <https://doi.org/10.1016/j.envpol.2021.117972>
- Blaise, C., Gagné, F., Harwood, M., Quinn, B., & Hanana, H. (2018). Ecotoxicity responses of the freshwater cnidarian *Hydra attenuata* to 11 rare earth elements. *Ecotoxicology and Environmental Safety*, 163(July), 486–491. <https://doi.org/10.1016/j.ecoenv.2018.07.033>
- Bonnail, E., Pérez-López, R., Sarmiento, A. M., Nieto, J. M., & DelValls, T. Á. (2017). A novel approach for acid mine drainage pollution biomonitoring using rare earth elements bioaccumulated in the freshwater clam *Corbicula fluminea*. *Journal of Hazardous Materials*, 338, 466–471. <https://doi.org/10.1016/j.jhazmat.2017.05.052>
- Boukadida, K., Banni, M., Gourves, P. Y., & Cachot, J. (2016). High sensitivity of embryo-larval stage of the Mediterranean mussel, *Mytilus galloprovincialis* to metal pollution in combination with temperature increase. *Marine Environmental Research*, 122, 59–66. <https://doi.org/10.1016/j.marenvres.2016.09.007>
- Brantley, S. L., Liermann, L. J., Bau, M., & Wu, S. (2001). Uptake of trace metals and rare earth elements from hornblende by a soil bacterium. *Geomicrobiology Journal*, 18(1), 37–61. <https://doi.org/10.1080/01490450151079770>
- Brewer, A., Dror, I., & Berkowitz, B. (2022). Electronic waste as a source of rare earth element pollution: Leaching, transport in porous media, and the effects of nanoparticles. *Chemosphere*, 287, 132217. <https://doi.org/10.1016/j.chemosphere.2021.132217>
- Bright, C. A., Cruse, A. M., Lyons, T. W., MacLeod, K. G., Glascock, M. D., & Ethington, R. L. (2009). Seawater rare-earth element patterns preserved in apatite of Pennsylvanian conodonts? *Geochimica et Cosmochimica Acta*, 73(6), 1609–1624. <https://doi.org/10.1016/j.gca.2008.12.014>
- Brioschi, L., Steinmann, M., Lucot, E., Pierret, M. C., Stille, P., Prunier, J., & Badot, P. M. (2013). Transfer of rare earth elements (REE) from natural soil to plant systems: Implications for the environmental availability of anthropogenic REE. *Plant and Soil*, 366(1–2), 143–163. <https://doi.org/10.1007/s11104-012-1407-0>
- Brito, P., Caetano, M., Martins, M. D., & Caçador, I. (2021). Effects of salt marsh plants on mobility and bioavailability of REE in estuarine sediments. *Science of the Total Environment*, 759, 144314. <https://doi.org/10.1016/j.scitotenv.2020.144314>
- Brito, P., Cesário, R., & Monteiro, C. E. S. (2020). Lesser-known metals with potential impacts in the marine environment. In *Coastal and deep ocean pollution* (pp. 215–247). CRC Press. <https://doi.org/10.1201/978203704271-10>
- Brito, P., Malvar, M., Galinha, C., Caçador, I., Canário, J., Araújo, M. F., & Raimundo, J. (2018). Yttrium and rare earth elements fractionation in salt marsh halophyte plants. *Science of the Total Environment*, 643, 1117–1126. <https://doi.org/10.1016/j.scitotenv.2018.06.291>
- Brito, P., Mil-Homens, M., Caçador, I., & Caetano, M. (2020). Changes in REE fractionation induced by the halophyte plant *Halimione portulacoides*, from SW European salt marshes. *Marine Chemistry*, 223(November 2019), 103805. <https://doi.org/10.1016/j.marchem.2020.103805>
- Brito, P., Prego, R., Mil-homens, M., Caçador, I., & Caetano, M. (2018). Sources and distribution of yttrium and rare earth elements in surface sediments from Tagus estuary, Portugal. *Science of the Total Environment*, 621, 317–325. <https://doi.org/10.1016/j.scitotenv.2017.11.245>
- Bruni, J., Canepa, M., Chiodini, G., Cioni, R., Cipolli, F., Longinelli, A., et al. (2002). Irreversible water-rock mass transfer accompanying the generation of the neutral, Mg-HCO<sub>3</sub> and high-pH, Ca-OC spring waters of the Genova province, Italy. *Applied Geochemistry*, 17(4), 455–474. [https://doi.org/10.1016/S0883-2927\(01\)00113-5](https://doi.org/10.1016/S0883-2927(01)00113-5)
- Brünjes, R., & Hofmann, T. (2020). Anthropogenic gadolinium in freshwater and drinking water systems. *Water Research*, 182, 115966. <https://doi.org/10.1016/j.watres.2020.115966>
- Bruno, J. (1997). Trace element modelling. In I. Grenthe & I. Puidomenech (Eds.), *Modelling in aquatic chemistry, Modelling in aquatic chemistry* (pp. 593–621).
- Butler, A. (1998). Acquisition and utilization of transition metal ions by marine organisms. *Science*, 281(5374), 207–209. <https://doi.org/10.1126/science.281.5374.207>
- Byrne, R. H. (2002). Speciation in seawater. In A. M. Ure & C. M. Davidson (Eds.), *Chemical speciation in the environment* (2nd ed., pp. 322–357). Blackwell Science.
- Byrne, R. H., & Kim, K. H. (1990). Rare earth element scavenging in seawater. *Geochimica et Cosmochimica Acta*, 54(10), 2645–2656. [https://doi.org/10.1016/0016-7037\(90\)90002-3](https://doi.org/10.1016/0016-7037(90)90002-3)
- Byrne, R. H., & Liu, X. (1998). A coupled riverine-marine fractionation model for dissolved rare earths and yttrium. *Aquatic Geochemistry*, 4(1), 103–121. <https://doi.org/10.1023/A:1009651919911>
- Byrne, R. H., & Sholkovitz, E. R. (1996). Marine chemistry and geochemistry of the lanthanides. In K. A. Gschneidner Jr. & L. Eyring (Eds.), *Handbook on the physics and chemistry of rare earths* (Vol. 23, pp. 497–593). Elsevier. [https://doi.org/10.1016/s0168-1273\(96\)23009-0](https://doi.org/10.1016/s0168-1273(96)23009-0)
- Cabral, H., Fonseca, V., Sousa, T., & Leal, M. C. (2019). Synergistic effects of climate change and marine pollution: An overlooked interaction in coastal and estuarine areas. *International Journal of Environmental Research and Public Health*, 16(15), 1–17. <https://doi.org/10.3390/ijerph16152737>

- Caçador, I., Caetano, M., Duarte, B., & Vale, C. (2009). Stock and losses of trace metals from salt marsh plants. *Marine Environmental Research*, 67(2), 75–82. <https://doi.org/10.1016/j.marenvres.2008.11.004>
- Caetano, M., Falcão, M., Vale, C., & Bebianno, M. J. (1997). Tidal flushing of ammonium, iron and manganese from inter-tidal sediment pore waters. *Marine Chemistry*, 58(1–2), 203–211. [https://doi.org/10.1016/S0304-4203\(97\)00035-2](https://doi.org/10.1016/S0304-4203(97)00035-2)
- Caetano, M., Vale, C., Cesário, R., & Fonseca, N. (2008). Evidence for preferential depths of metal retention in roots of salt marsh plants. *Science of the Total Environment*, 390(2–3), 466–474. <https://doi.org/10.1016/j.scitotenv.2007.10.015>
- Campbell, P. (1995). Interactions between trace metals and organisms: Critique of the free-ion activity model. In Willey (Ed.), *Metal speciation and bioavailability in aquatic systems*. (pp. 45–102).
- Cantrell, K. J., & Byrne, R. H. (1987). Rare earth element complexation by carbonate and oxalate ions. *Geochimica et Cosmochimica Acta*, 51(3), 597–605. [https://doi.org/10.1016/0016-7037\(87\)90072-X](https://doi.org/10.1016/0016-7037(87)90072-X)
- Cao, C., Liu, X.-M., Bataille, C. P., & Liu, C. (2020). What do Ce anomalies in marine carbonates really mean? A perspective from leaching experiments. *Chemical Geology*, 532, 119413. <https://doi.org/10.1016/j.chemgeo.2019.119413>
- Cao, C., Liu, X.-M., & Chen, J. (2022). Cerium anomaly as a tracer for paleo-oceanic redox conditions: A thermodynamics-based Ce oxidation modeling approach. *Frontiers in Earth Science*, 10, 927826. <https://doi.org/10.3389/feart.2022.927826>
- Carr, S. A., Liu, J., & Tesoro, A. G. (2016). Transport and fate of microplastic particles in wastewater treatment plants. *Water Research*, 91, 174–182. <https://doi.org/10.1016/j.watres.2016.01.002>
- Castor, S. B., & Hedrick, J. B. (2006). Rare earth elements. *Industrial Minerals and Rocks*, 7, 769–792.
- Censi, P., Spoto, S. E., Nardone, G., Saiano, F., Punturo, R., Di Geronimo, S. I., et al. (2005). Rare-earth elements and yttrium distributions in mangrove coastal water systems: The western Gulf of Thailand. *Chemistry and Ecology*, 21(4), 255–277. <https://doi.org/10.1080/02757540500213216>
- Cervini-Silva, J., Fowle, D. A., & Banfield, J. (2005). Biogenic dissolution of a soil cerium-phosphate mineral. *American Journal of Science*, 305(6–8 SPEC. ISS.), 711–726. <https://doi.org/10.2475/ajs.305.6-8.711>
- Cervini-Silva, J., Gilbert, B., Fakra, S., Friedlich, S., & Banfield, J. (2008). Coupled redox transformations of catechol and cerium at the surface of a cerium(III) phosphate mineral. *Geochimica et Cosmochimica Acta*, 72(10), 2454–2464. <https://doi.org/10.1016/j.gca.2008.02.017>
- Chakraborty, P., Babu, P. R., & Sarma, V. V. (2011). A multi-method approach for the study of lanthanum speciation in coastal and estuarine sediments. *Journal of Geochemical Exploration*, 110(2), 225–231. <https://doi.org/10.1016/j.gexplo.2011.05.013>
- Chapelle, F., & Knobel, L. (1983). Aqueous geochemistry and exchangeable cation composition of glauconite in the Aquia aquifer, Maryland. *Ground Water*, 21(3), 343–352. <https://doi.org/10.1111/j.1745-6584.1983.tb00734.x>
- Chapman, P. M., Allen, H. E., Godfredsen, K., & Z'Graggen, M. N. (1996). Policy analysis, peer reviewed: Evaluation of bioaccumulation factors in regulating metals. *Environmental Science & Technology*, 30(10), 448A–452A. <https://doi.org/10.1021/es962436d>
- Chavagnac, V., Monnin, C., Ceuleneer, G., Boulart, C., & Hoareau, G. (2013). Characterization of hyperalkaline fluids produced by low-temperature serpentinization of mantle peridotites in the Oman and Ligurian ophiolites. *Geochemistry, Geophysics, Geosystems*, 14(7), 2496–2522. <https://doi.org/10.1002/ggge.20147>
- Chavagnac, V., Saleban Ali, H., Jeandel, C., Leleu, T., Destigneville, C., Castillo, A., et al. (2018). Sulfate minerals control dissolved rare earth element flux and Nd isotope signature of buoyant hydrothermal plume (EMSO-Azores, 37°N Mid-Atlantic Ridge). *Chemical Geology*, 499, 111–125. <https://doi.org/10.1016/j.chemgeo.2018.09.021>
- Chevis, D. A., Johannesson, K. H., Burdige, D. J., Cable, J. E., Martin, J. B., & Roy, M. (2015). Rare earth element cycling in a sandy subterranean estuary in Florida, USA. *Marine Chemistry*, 176, 34–50. <https://doi.org/10.1016/j.marchem.2015.07.003>
- Chevis, D. A., Johannesson, K. H., Burdige, D. J., Tang, J., Bradley Moran, S., & Kelly, R. P. (2015). Submarine groundwater discharge of rare earth elements to a tidally-mixed estuary in Southern Rhode Island. *Chemical Geology*, 397, 128–142. <https://doi.org/10.1016/j.chemgeo.2015.01.013>
- Chevis, D. A., Mohajerin, T. J., Yang, N., Cable, J. E., Rasbury, E. T., Hemming, S. R., et al. (2021). Neodymium Isotope Geochemistry of a Subterranean Estuary. *Frontiers in Water*, 3(November), 1–21. <https://doi.org/10.3389/frwa.2021.778344>
- Chistoserdova, L. (2016). Lanthanides: New life metals? *World Journal of Microbiology and Biotechnology*, 32(8), 1–7. <https://doi.org/10.1007/s11274-016-2088-2>
- Choppin, G. R. (1983). Comparison of the solution chemistry of the actinides and lanthanides. *Journal of the Less-Common Metals*, 93(2), 323–330. [https://doi.org/10.1016/0022-5088\(83\)90177-7](https://doi.org/10.1016/0022-5088(83)90177-7)
- Chour, Z., Laubie, B., Morel, J. L., Tang, Y. T., Simonnot, M. O., & Muhr, L. (2020). Basis for a new process for producing REE oxides from *Dicranopteris linearis*. *Journal of Environmental Chemical Engineering*, 8(4), 103961. <https://doi.org/10.1016/j.jece.2020.103961>
- Christenson, E. A., & Schijf, J. (2011). Stability of YREE complexes with the trihydroxamate siderophore desferrioxamine B at seawater ionic strength. *Geochimica et Cosmochimica Acta*, 75(22), 7047–7062. <https://doi.org/10.1016/j.gca.2011.09.022>
- Cooley, S., Schoeman, D., Bopp, L., Boyd, P., Donner, S., Ghebrehiwet, Y., et al. (2022). Oceans and coastal ecosystems and their services supplementary material. climate change 2022: Impacts, adaptation and vulnerability. contribution of working group II. In H. O. Pörtner, D. Roberts, M. Tignor, et al. (Eds.), *Sixth assessment report of the Intergovernmental Panel on Climate Change*.
- Costa, L., Johannesson, K., Mirlean, N., & Quintana, G. (2021). Rare earth element distributions in salt marsh sediment cores reveal evidence of environmental lability during bioturbation and diagenetic processes. *Chemical Geology*, 584, 120503. <https://doi.org/10.1016/j.chemgeo.2021.120503>
- Costa, L., Mirlean, N., & Johannesson, K. (2021). Rare earth elements as tracers of sediment contamination by fertilizer industries in Southern Brazil, Patos Lagoon Estuary. *Applied Geochemistry*, 129(February), 104965. <https://doi.org/10.1016/j.apgeochem.2021.104965>
- Costa, M., Henriques, B., Pinto, J., Fabre, E., Dias, M., Soares, J., et al. (2020). Influence of toxic elements on the simultaneous uptake of rare earth elements from contaminated waters by estuarine macroalgae. *Chemosphere*, 252, 126562. <https://doi.org/10.1016/j.chemosphere.2020.126562>
- Cotruvo, J. A., Jr., Featherston, E. R., Mattocks, J. A., Ho, J. V., & Laremore, T. N. (2018). Lanmodulin: A highly selective lanthanide-binding protein from a lanthanide-utilizing bacterium. *Journal of the American Chemical Society*, 140(44), 15056–15061. <https://doi.org/10.1021/jacs.8b09842>
- Crockett, K. C., Hill, E., Abell, R. E., Johnson, C., Gary, S. F., Brand, T., & Hathorne, E. C. (2018). Rare earth element distribution in the NE Atlantic: Evidence for benthic sources, longevity of the seawater signal, and biogeochemical cycling. *Frontiers in Marine Science*, 5, 147. <https://doi.org/10.3389/fmars.2018.00147>
- Daumann, L. J. (2019). Essential and ubiquitous: The emergence of lanthanide metallobiochemistry. *Angewandte Chemie International Edition*, 58(37), 12795–12802. <https://doi.org/10.1002/anie.201904090>
- Davranche, M., Grybos, M., Gruau, G., Pédrot, M., Dia, A., & Marsac, R. (2011). Rare earth element patterns: A tool for identifying trace metal sources during wetland soil reduction. *Chemical Geology*, 284(1–2), 127–137. <https://doi.org/10.1016/j.chemgeo.2011.02.014>

- Davranche, M., Pourret, O., Gruau, G., & Dia, A. (2004). Impact of humate complexation on the adsorption of REE onto Fe oxyhydroxide. *Journal of Colloid and Interface Science*, 277(2), 271–279. <https://doi.org/10.1016/j.jcis.2004.04.007>
- Davranche, M., Pourret, O., Gruau, G., Dia, A., & Le Coz-Bouhnik, M. (2005). Adsorption of REE (III)-humate complexes onto MnO<sub>2</sub>: Experimental evidence for cerium anomaly and lanthanide tetrad effect suppression. *Geochimica et Cosmochimica Acta*, 69(20), 4825–4835. <https://doi.org/10.1016/j.gca.2005.06.005>
- de Baar, H. J. W., Bacon, M. P., & Brewer, P. G. (1983). Rare-earth distributions with a positive Ce anomaly in the Western North Atlantic Ocean. *Nature*, 301, 324–328. <https://doi.org/10.1038/301324a0>
- de Baar, H. J. W., Bruland, K. W., Schijf, J., van Heuven, S. M. A. C., & Behrens, M. K. (2018). Low cerium among the dissolved rare earth elements in the central North Pacific Ocean. *Geochimica et Cosmochimica Acta*, 236, 5–40. <https://doi.org/10.1016/j.gca.2018.03.003>
- de Baar, H. J. W., German, C. R., Elderfield, H., & van Gaans, P. (1988). Rare earth element distributions in anoxic waters of the Cariaco Trench. *Geochimica et Cosmochimica Acta*, 52(5), 1203–1219. [https://doi.org/10.1016/0016-7037\(88\)90275-X](https://doi.org/10.1016/0016-7037(88)90275-X)
- De Carlo, E. H., Wen, X. Y., & Irving, M. (1997). The influence of redox reactions on the uptake of dissolved Ce by suspended Fe and Mn oxide particles. *Aquatic Geochemistry*, 3(4), 357–389. <https://doi.org/10.1023/A:1009664626181>
- de Chanvalon, A. T., Metzger, E., Mouret, A., Knoery, J., Chiffolleau, J., & Brach-papa, C. (2016). Particles transformation in estuaries: Fe, Mn and REE signatures through the Loire Estuary. *Journal of Sea Research*, 118, 103–112. <https://doi.org/10.1016/j.seares.2016.11.004>
- de Freitas, T. O. P., Pedreira, R. M. A., & Hatje, V. (2021). Distribution and fractionation of rare earth elements in sediments and mangrove soil profiles across an estuarine gradient. *Chemosphere*, 264, 128431. <https://doi.org/10.1016/j.chemosphere.2020.128431>
- Delgado, J., Pérez-López, R., Galván, L., Nieto, J. M., & Boski, T. (2012). Enrichment of rare earth elements as environmental tracers of contamination by acid mine drainage in salt marshes: A new perspective. *Marine Pollution Bulletin*, 64(9), 1799–1808. <https://doi.org/10.1016/j.marpolbul.2012.06.001>
- Deng, G., Ma, T., Tanaka, K., Ohnuki, T., Qiu, X., & Yu, Q. (2020). Saccharide-mediated transformation of Ce during the formation of manganese (hydr)oxide. *Geochimica et Cosmochimica Acta*, 286, 143–158. <https://doi.org/10.1016/j.gca.2020.07.028>
- Deng, K., Yang, S., Du, J., Lian, E., & Vance, D. (2022). Dominance of benthic flux of REEs on continental shelves: Implications for oceanic budgets. *Geochemical Perspectives Letters*, 22, 26–30. <https://doi.org/10.7185/geochemlet.2223>
- Deng, Y., Ren, J., Guo, Q., Cao, J., Wang, H., & Liu, C. (2017). Rare earth element geochemistry characteristics of seawater and porewater from deep sea in western Pacific. *Scientific Reports*, 7(1), 1–13. <https://doi.org/10.1038/s41598-017-16379-1>
- de Sena, I. M., Souza, L. A., Patire, V. F., Arias-Ortiz, A., Creed, J. C., Cruz, I., & Hatje, V. (2022). Environmental Settings of Seagrass Meadows Control Rare Earth Element Distribution and Transfer from Soil to Plant Compartments. *SSRN Electronic Journal*, 843(June). <https://doi.org/10.2139/ssrn.4081360>
- Dia, A., Gruau, G., Olivie-Lauquet, G., Riou, C., Molénat, J., & Curmi, P. (2000). The distribution of rare earth elements in groundwaters: Assessing the role of source-rock composition, redox changes and colloidal particles. *Geochimica et Cosmochimica Acta*, 64(24), 4131–4151. [https://doi.org/10.1016/S0016-7037\(00\)00494-4](https://doi.org/10.1016/S0016-7037(00)00494-4)
- Ding, Y., Sun, W., Liu, S., Xie, J., Tang, D., Zhou, X., et al. (2022). Low oxygen levels with high redox heterogeneity in the late Ediacaran shallow ocean: Constraints from I/(Ca + Mg) and Ce/Ce\* of the Dengying Formation, South China. *Geobiology*, 20(6), 790–809. <https://doi.org/10.1111/gbi/12520>
- Du, J., Haley, B. A., Mix, A. C., Abbott, A. N., McManus, J., & Vance, D. (2022). Reactive-transport modeling of neodymium and its radiogenic isotope in deep-sea sediments: The roles of authigenesis, marine silicate weathering and reverse weathering. *Earth and Planetary Science Letters*, 596, 117792. <https://doi.org/10.1016/j.epsl.2022.117792>
- Duddy, I. R. (1980). Redistribution and fractionation of rare-earth and other elements in a weathering profile. *Chemical Geology*, 30(4), 363–381. [https://doi.org/10.1016/0009-2541\(80\)90102-3](https://doi.org/10.1016/0009-2541(80)90102-3)
- Dulski, P. (1994). Interferences of oxide, hydroxide and chloride analyte species in the determination of rare earth elements in geological samples by inductively coupled plasma-mass spectrometry. *Fresenius' Journal of Analytical Chemistry*, 350(4–5), 194–203. <https://doi.org/10.1007/BF00322470>
- Duncan, T., & Shaw, T. J. (2003). The mobility of rare earth elements and redox sensitive elements in the groundwater/seawater mixing zone of a shallow coastal aquifer. *Aquatic Geochemistry*, 9(3), 233–255. <https://doi.org/10.1023/B:AQUA.0000022956.20338.26>
- Duvert, C., Cendón, D. I., Raiber, M., Seidel, J. L., & Cox, M. E. (2015). Seasonal and spatial variations in rare earth elements to identify inter-aquifer linkages and recharge processes in an Australian catchment. *Chemical Geology*, 396, 83–97. <https://doi.org/10.1016/j.chemgeo.2014.12.022>
- Eckert, J. M., & Sholkovitz, E. R. (1976). The flocculation of iron, aluminium and humates from river water by electrolytes. *Geochimica et Cosmochimica Acta*, 40(7), 847–848. [https://doi.org/10.1016/0016-7037\(76\)90036-3](https://doi.org/10.1016/0016-7037(76)90036-3)
- Elderfield, H. (1988). The oceanic chemistry of the rare-earth elements. *Philosophical Transactions of the Royal Society of London*, 325(1583), 105–126. <https://doi.org/10.1098/rsta.1988.0046>
- Elderfield, H. (2002). Foraminiferal Mg/Ca paleothermometry: Expected advances and unexpected consequences. *12th Annual V.M. Goldschmidt Conference*, 66, A213.
- Elderfield, H., & Greaves, M. J. (1981). Negative cerium anomalies in the rare earth element patterns of oceanic ferromanganese nodules. *Earth and Planetary Science Letters*, 55(1), 163–170. [https://doi.org/10.1016/0012-821X\(81\)90095-9](https://doi.org/10.1016/0012-821X(81)90095-9)
- Elderfield, H., & Greaves, M. J. (1982). The rare earth elements in seawater. *Nature*, 296(5854), 214–219. <https://doi.org/10.1038/296214a0>
- Elderfield, H., & Sholkovitz, E. R. (1987). Rare earth elements in the pore waters of reducing nearshore sediments. *Earth and Planetary Science Letters*, 82(3–4), 280–288. [https://doi.org/10.1016/0012-821X\(87\)90202-0](https://doi.org/10.1016/0012-821X(87)90202-0)
- Elderfield, H., Upstill-Goddard, R., & Sholkovitz, E. R. (1990). The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta*, 54(4), 971–991. [https://doi.org/10.1016/0016-7037\(90\)90432-K](https://doi.org/10.1016/0016-7037(90)90432-K)
- Elderfield, H., Whitfield, M., Burton, J. D., Bacon, M. P., & Liss, P. S. (1988). The oceanic chemistry of the rare-earth elements. *Philosophical Transactions of the Royal Society of London - Series A: Mathematical and Physical Sciences*, 325, 105–126. <https://doi.org/10.1098/rsta.1988.0046>
- El Zrelli, R., Baliteau, J. Y., Yacoubi, L., Castet, S., Grégoire, M., Fabre, S., et al. (2021). Rare earth elements characterization associated to the phosphate fertilizer plants of Gabes (Tunisia, Central Mediterranean Sea): Geochemical properties and behavior, related economic losses, and potential hazards. *Science of the Total Environment*, 791, 148268. <https://doi.org/10.1016/j.scitotenv.2021.148268>
- Espejo, W., Chiang, G., Kitamura, D., Kashiwada, S., O'Driscoll, N. J., & Celis, J. E. (2023). Occurrence of rare earth elements (REEs) and trace elements (TEs) in feathers of adult and young Gentoo penguins from King George Island, Antarctica. *Marine Pollution Bulletin*, 187(January), 1–6. <https://doi.org/10.1016/j.marpolbul.2023.114575>
- Evans, J., DeHart, M., Weaver, K., & Keiser, D., Jr. (2022). Burnable absorbers in nuclear reactors – A review. *Nuclear Engineering and Design*, 391, 111726. <https://doi.org/10.1016/j.nucengdes.2022.111726>



- Farmer, D. (1996). *Investigation of regional flow patterns in the Ash Meadows ground-water basin of southern Nevada using uranium isotope ratios*. University of Nevada, Las Vegas.
- Fee, J. A., Gaudette, H. E., Lyons, W. B., & Long, D. T. (1992). Rare-earth element distribution in Lake Tyrrell groundwaters, Victoria, Australia. *Chemical Geology*, 96(1–2), 67–93. [https://doi.org/10.1016/0009-2541\(92\)90122-L](https://doi.org/10.1016/0009-2541(92)90122-L)
- Figueiredo, C., Grilo, T., Oliveira, R., Ferreira, I., Gil, F., Lopes, C., et al. (2022). Single and combined ecotoxicological effects of ocean warming, acidification and lanthanum exposure on the surf clam (*Spisula solida*). *Chemosphere*, 303, 134850. <https://doi.org/10.1016/j.chemosphere.2022.134850>
- Filippova, A., Frank, M., Kienast, M., Rickli, J., Hathorne, E., Yashayaev, I. M., & Pahnke, K. (2017). Water mass circulation and weathering inputs in the Labrador Sea based on coupled Hf–Nd isotope compositions and rare earth element distributions. *Geochimica et Cosmochimica Acta*, 199, 164–184. <https://doi.org/10.1016/j.gca.2016.11.024>
- Flynn, T. M., Sanford, R. A., Santo Domingo, J. W., Ashbolt, N. J., Levine, A. D., & Bethke, C. M. (2012). The active bacterial community in a pristine confined aquifer. *Water Resources Research*, 48(9), 1–10. <https://doi.org/10.1029/2011WR011568>
- Fox, L. E. (1983). The removal of dissolved humic acid during estuarine mixing. *Estuarine, Coastal and Shelf Science*, 16(4), 431–440. [https://doi.org/10.1016/0272-7714\(83\)90104-X](https://doi.org/10.1016/0272-7714(83)90104-X)
- Frank, M. (2002). Radiogenic isotopes: Tracers of past ocean circulation and erosional input. *Reviews of Geophysics*, 40(1), 1. <https://doi.org/10.1029/2000RG000094>
- Freitas, R., Costa, S., Cardoso, C. E., Morais, T., Moleiro, P., Matias, A. C., et al. (2020). Toxicological effects of the rare earth element neodymium in *Mytilus galloprovincialis*. *Chemosphere*, 244, 125457. <https://doi.org/10.1016/j.chemosphere.2019.125457>
- Freslon, N., Bayon, G., Toucanne, S., Bernell, S., Bollinger, C., Chéron, S., et al. (2014). Rare earth elements and neodymium isotopes in sedimentary organic matter. *Geochimica et Cosmochimica Acta*, 140, 177–198. <https://doi.org/10.1016/j.gca.2014.05.016>
- Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., et al. (1979). Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochimica et Cosmochimica Acta*, 43(7), 1075–1090. [https://doi.org/10.1016/0016-7037\(79\)90095-4](https://doi.org/10.1016/0016-7037(79)90095-4)
- Gammons, C. H. (2002). Complexation of the rare earth elements with aqueous chloride at 200°C and 300°C and saturated water vapor pressure. *Water-Rock Interaction, Ore Deposits, Environmental Geochemistry*, 7, 191–207.
- Gammons, C. H., Nimick, D. A., Parker, S. R., Cleasby, T. E., & McCleskey, R. B. (2005). Diel behavior of iron and other heavy metals in a mountain stream with acidic to neutral pH: Fisher Creek, Montana, USA. *Geochimica et Cosmochimica Acta*, 69(10), 2505–2516. <https://doi.org/10.1016/j.gca.2004.11.020>
- Gammons, C. H., Wood, S. A., & Williams-Jones, A. E. (1996). The aqueous geochemistry of the rare earth elements and yttrium: VI. Stability of neodymium chloride complexes from 25 to 300°C. *Geochimica et Cosmochimica Acta*, 60(23), 4615–4630. [https://doi.org/10.1016/S0016-7037\(96\)00262-1](https://doi.org/10.1016/S0016-7037(96)00262-1)
- García-Solsona, E., & Jeandel, C. (2020). Balancing rare earth element distributions in the Northwestern Mediterranean Sea. *Chemical Geology*, 532, 119372. <https://doi.org/10.1016/j.chemgeo.2019.119372>
- García-Solsona, E., Jeandel, C., Labatut, M., Lacan, F., Vance, D., Chavagnac, V., & Pradoux, C. (2014). Rare earth elements and Nd isotopes tracing water mass mixing and particle-seawater interactions in the SE Atlantic. *Geochimica et Cosmochimica Acta*, 125, 351–372. <https://doi.org/10.1016/j.gca.2013.10.009>
- Geagea, M. L., Stille, P., Gauthier-Lafaye, F., & Millet, M. (2007). Tracing of industrial emissions in an urban environment using Pb, Sr, Nd, and C isotopes (tree bark biomonitoring and aerosol sampling). *Geochimica et Cosmochimica Acta*, 71(15, S), A537. <https://doi.org/10.1021/es071704c>
- German, C. R., & Elderfield, H. (1989). Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin. *Geochimica et Cosmochimica Acta*, 53(10), 2561–2571. [https://doi.org/10.1016/0016-7037\(89\)90128-2](https://doi.org/10.1016/0016-7037(89)90128-2)
- German, C. R., & Elderfield, H. (1990). Application of the Ce anomaly as a paleoredox indicator: The ground rules. *Paleoceanography*, 5(5), 823–833. <https://doi.org/10.1029/PA005i005p00823>
- German, C. R., Holliday, B. P., & Elderfield, H. (1991). Redox cycling of rare earth elements in the suboxic zone of the Black Sea. *Geochimica et Cosmochimica Acta*, 55(12), 3553–3558. [https://doi.org/10.1016/0016-7037\(91\)90055-A](https://doi.org/10.1016/0016-7037(91)90055-A)
- Goldstein, S. J., & Jacobsen, S. (1987). The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in seawater. *Chemical Geology*, 66(3–4), 245–272. [https://doi.org/10.1016/0168-9622\(87\)90045-5](https://doi.org/10.1016/0168-9622(87)90045-5)
- Goldstein, S. J., & Jacobsen, S. (1988a). REE in the Great Whale River estuary, northwest Quebec. *Earth and Planetary Science Letters*, 88(3–4), 241–252. [https://doi.org/10.1016/0012-821X\(88\)90081-7](https://doi.org/10.1016/0012-821X(88)90081-7)
- Goldstein, S. J., & Jacobsen, S. B. (1988b). Rare earth elements in river waters. *Earth and Planetary Science Letters*, 89(1), 35–47. [https://doi.org/10.1016/0012-821X\(88\)90031-3](https://doi.org/10.1016/0012-821X(88)90031-3)
- Goldstein, S. L., & Hemming, S. R. (2003). Long-lived isotopic tracers in oceanography, paleoceanography, and ice-sheet dynamics. *Treatise on geochemistry*, 6, 453–483. <https://doi.org/10.1016/B978-0-08-095975-7.00617-3>
- Goldstein, S. L., O'niions, R. K., & Hamilton, P. J. (1984). A Sm–Nd isotopic study of atmospheric dusts and particulates from major river systems. *Earth and Planetary Science Letters*, 70(2), 221–236. [https://doi.org/10.1016/0012-821X\(84\)90007-4](https://doi.org/10.1016/0012-821X(84)90007-4)
- Gomes, P., Valente, T., Marques, R., Prudêncio, M. I., & Pamplona, J. (2022). Rare earth elements - Source and evolution in an aquatic system dominated by mine-Influenced waters. *Journal of Environmental Management*, 322(July), 116125. <https://doi.org/10.1016/j.jenvman.2022.116125>
- Gonzalez, V., Vignati, D. A. L., Leyval, C., & Giamberini, L. (2014). Environmental fate and ecotoxicity of lanthanides: Are they a uniform group beyond chemistry? *Environment International*, 71, 148–157. <https://doi.org/10.1016/j.envint.2014.06.019>
- Gosselin, D. C., Smith, M. R., Lepel, E. A., & Laul, J. C. (1992). Rare earth elements in chloride-rich groundwater, Palo Duro Basin, Texas, USA. *Geochimica et Cosmochimica Acta*, 56(4), 1495–1505. [https://doi.org/10.1016/0016-7037\(92\)90219-9](https://doi.org/10.1016/0016-7037(92)90219-9)
- Grenier, M., Jeandel, C., Lacan, F., Vance, D., Venchiarutti, C., Cros, A., & Cravatte, S. (2013). From the subtropics to the central equatorial Pacific Ocean: Neodymium isotopic composition and rare earth element concentration variations. *Journal of Geophysical Research: Oceans*, 118(2), 592–618. <https://doi.org/10.1029/2012JC008239>
- Gu, S., Liu, Z., Jahn, A., Rempfer, J., Zhang, J., & Joos, F. (2017). Neodymium isotopes in the ocean model of the Community Earth System 2 Model (CESM1.3). *Geoscientific Model Development Discussions*, 2, 1–41. <https://doi.org/10.5194/gmd-2017-40>
- Guichard, F., Church, T. M., Treuil, M., & Jaffrezic, H. (1979). Rare earths in barites: Distribution and effects on aqueous partitioning. *Geochimica et Cosmochimica Acta*, 43(7), 983–997. [https://doi.org/10.1016/0016-7037\(79\)90088-7](https://doi.org/10.1016/0016-7037(79)90088-7)
- Guo, C., Wei, Y., Yan, L., Li, Z., Qian, Y., Liu, H., et al. (2020). Rare earth elements exposure and the alteration of the hormones in the hypothalamic-pituitary-thyroid (HPT) axis of the residents in an e-waste site: A cross-sectional study. *Chemosphere*, 252, 126488. <https://doi.org/10.1016/j.chemosphere.2020.126488>

- Guo, Q., Shields, G. A., Liu, C., Strauss, H., Zhu, M., Pi, D., et al. (2007). Trace element chemostratigraphy of two Ediacaran-Cambrian successions in South China: Implications for organosedimentary metal enrichment and silicification in the early Cambrian. *Palaeoceanography, Palaeoclimatology, Palaeoecology*, 254(1–2), 194–216. <https://doi.org/10.1016/j.palaeo.2007.03.016>
- Gwenzi, W., Mangori, L., Danha, C., Chaukura, N., Dunjana, N., & Sanganyado, E. (2018). Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants. *Science of the Total Environment*, 636, 299–313. <https://doi.org/10.1016/j.scitotenv.2018.04.235>
- Gwynn, J. P., Hatje, V., Casacuberta, N., Sarin, M., & Osvath, I. (2024). The effect of climate change on sources of radionuclides to the marine environment. *Communications Earth & Environment*, 5(1), 135. <https://doi.org/10.1038/s43247-024-01241-w>
- Haas, J. R., Shock, E. L., & Sassani, D. C. (1995). Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. *Geochimica et Cosmochimica Acta*, 59(21), 4329–4350. [https://doi.org/10.1016/0016-7037\(95\)00314-P](https://doi.org/10.1016/0016-7037(95)00314-P)
- Haley, B. A., Du, J., Abbott, A. N., & McManus, J. (2017). The Impact of Benthic Processes on Rare Earth Element and Neodymium Isotope Distributions in the Oceans. *Frontiers in Marine Science*, 4(December), 1–12. <https://doi.org/10.3389/fmars.2017.00426>
- Haley, B. A., Frank, M., Hathorne, E., & Pisiadis, N. (2014). Biogeochemical implications from dissolved rare earth element and Nd isotope distributions in the Gulf of Alaska. *Geochimica et Cosmochimica Acta*, 126, 455–474. <https://doi.org/10.1016/j.gca.2013.11.012>
- Haley, B. A., & Klinkhammer, G. P. (2003). Complete separation of rare earth elements from small volume seawater samples by automated ion chromatography: Method development and application to benthic flux. *Marine Chemistry*, 82(3–4), 197–220. [https://doi.org/10.1016/S0304-4203\(03\)00070-7](https://doi.org/10.1016/S0304-4203(03)00070-7)
- Haley, B. A., Klinkhammer, G. P., & McManus, J. (2004). Rare earth elements in pore waters of marine sediments. *Geochimica et Cosmochimica Acta*, 68(6), 1265–1279. <https://doi.org/10.1016/j.gca.2003.09.012>
- Haley, B. A., Wu, Y., Muratli, J. M., Basak, C., Pena, L. D., & Goldstein, S. L. (2021). Rare earth element and neodymium isotopes of the eastern US GEOTRACES Equatorial Pacific Zonal Transect (GP16). *Earth and Planetary Science Letters*, 576, 117233. <https://doi.org/10.1016/j.epsl.2021.117233>
- Hannigan, R., Dorval, E., & Jones, C. (2010). The rare earth element chemistry of estuarine surface sediments in the Chesapeake Bay. *Chemical Geology*, 272(1–4), 20–30. <https://doi.org/10.1016/j.chemgeo.2010.01.009>
- Hannigan, R. E., & Sholkovitz, E. R. (2001). The development of middle rare earth element enrichments in freshwaters: Weathering of phosphate minerals. *Chemical Geology*, 175(3–4), 495–508. [https://doi.org/10.1016/S0009-2541\(00\)00355-7](https://doi.org/10.1016/S0009-2541(00)00355-7)
- Hao, Z., Li, Y., Li, H., Wei, B., Liao, X., Liang, T., & Yu, J. (2015). Levels of rare earth elements, heavy metals and uranium in a population living in Baiyun Obo, Inner Mongolia, China: A pilot study. *Chemosphere*, 128, 161–170. <https://doi.org/10.1016/j.chemosphere.2015.01.057>
- Hara, Y., Obata, H., Doi, T., Hongo, Y., Gamo, T., Takeda, S., & Tsuda, A. (2009). Rare earth elements in seawater during an iron-induced phytoplankton bloom of the western subarctic Pacific (SEEDS-II). *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(26), 2839–2851. <https://doi.org/10.1016/j.dsr2.2009.06.009>
- Haskin, L. A., Wideman, T. R., Frey, A. F., Collins, K. A., Keedy, C. R., & Haskin, M. A. (1966). Rare earths in sediments. *Journal of Geophysical Research*, 71(24), 6091–6105. <https://doi.org/10.1029/jz071i024p06091>
- Haskin, M. A., & Haskin, L. A. (1966). Rare earths in European shale: A redetermination. *Science*, 154(3748), 507–509. <https://doi.org/10.1126/science.154.3748.507>
- Hathorne, E. C., Stichel, T., Brück, B., & Frank, M. (2015). Rare earth element distribution in the Atlantic sector of the Southern Ocean: The balance between particle scavenging and vertical supply. *Marine Chemistry*, 177, 157–171. <https://doi.org/10.1016/j.marchem.2015.03.011>
- Hatje, V., Bruland, K. W., & Flegal, A. R. (2014). Determination of rare earth elements after pre-concentration using NOBIAS-chelate PA-1 resin: Method development and application in the San Francisco Bay plume. *Marine Chemistry*, 160, 34–41. <https://doi.org/10.1016/j.marchem.2014.01.006>
- Hatje, V., Bruland, K. W., & Flegal, A. R. (2016). Increases in Anthropogenic Gadolinium Anomalies and Rare Earth Element Concentrations in San Francisco Bay over a 20 Year Record. *Environmental Science and Technology*, 50(8), 4159–4168. <https://doi.org/10.1021/acs.est.5b04322>
- Hatje, V., Sarin, M., Sander, S. G., Ramachandran, P., Völker, C., Barra, R. O., & Tagliabue, A. (2022). Emergent interactive effects of climate change and contaminants in coastal and ocean ecosystems. *Frontiers in Marine Science*, 9(July), 1–8. <https://doi.org/10.3389/fmars.2022.936109>
- Haxel, G., Hedrick, J. B., Orris, G. J., Stauffer, P. H., & Hendley, J. W. (2002). Rare earth elements: Critical resources for high technology. *US Department of the Interior, US Geological Survey*, 87(2). <https://doi.org/10.3133/fs08702>
- Hein, J., Koschinsky, A., & Kuhn, T. (2020). Deep-ocean polymetallic nodules as a resource for critical materials. *Nature Reviews Earth & Environment*, 1(3), 158–169. <https://doi.org/10.1038/s43017-020-0027-0>
- Henríquez-hernández, L. A., Boada, L. D., Carranza, C., Pérez-arellano, J. L., González-antuña, A., Camacho, M., et al. (2017). Blood levels of toxic metals and rare earth elements commonly found in e-waste may exert subtle effects on hemoglobin concentration in sub-Saharan immigrants. *Environment International*, 109, 20–28. <https://doi.org/10.1016/j.envint.2017.08.023>
- Himmeler, T., Haley, B. A., Torres, M. E., Klinkhammer, G. P., Bohrmann, G., & Peckmann, J. (2013). Rare earth element geochemistry in cold-seep pore waters of Hydrate Ridge, northeast Pacific Ocean. *Geo-Marine Letters*, 33(5), 369–379. <https://doi.org/10.1007/s00367-013-0334-2>
- Hissler, C., Montarges-Pelletier, E., Kanbar, H. J., Le Meur, M., & Gauthier, C. (2023). Impact of past steel-making activities on lanthanides and Y (REY) fractionation and potential mobility in riverbank sediments. *Frontiers in Earth Science*, 10, 1–12. <https://doi.org/10.3389/feart.2022.1056919>
- Hissler, C., Stille, P., Franc, J., Laurent, P., Chabaux, F., & Pfister, L. (2016). Origin and Dynamics of Rare Earth Elements during Flood Events in Contaminated River Basins: Sr – Nd – Pb Isotopic Evidence. *Environmental Science & Technology*, 50(9), 4624–4631. <https://doi.org/10.1021/acs.est.5b03660>
- Hissler, C., Stille, P., Krein, A., Geagea, M. L., Perrone, T., Probst, J. L., & Hoffmann, L. (2008). Identifying the origins of local atmospheric deposition in the steel industry basin of Luxembourg using the chemical and isotopic composition of the lichen *Xanthoria parietina*. *Science of the Total Environment*, 405(1–3), 338–344. <https://doi.org/10.1016/j.scitotenv.2008.05.029>
- Hodel, F., Grespan, R., de Rafélis, M., Dera, G., Lezin, C., Nardin, E., et al. (2021). Drake Passage gateway opening and Antarctic Circumpolar Current onset 31 Ma ago: The message of foraminifera and reconsideration of the Neodymium isotope record. *Chemical Geology*, 570(November 2020), 120171. <https://doi.org/10.1016/j.chemgeo.2021.120171>
- Holsler, W. T. (1997). Evaluation of the application of rare-earth elements to paleoceanography. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 132(1–4), 309–323. [https://doi.org/10.1016/S0031-0182\(97\)00069-2](https://doi.org/10.1016/S0031-0182(97)00069-2)
- Hongo, Y., Obata, H., Gamo, T., Nakaseama, M., Ishibashi, J., Konno, U., et al. (2007). Rare earth elements in the hydrothermal system at Okinawa Trough back-arc basin. *Geochemical Journal*, 41, 1–15. <https://doi.org/10.2343/geochemj.41.1>

- Hoyle, J., Elderfield, H., Gledhill, A., & Greaves, M. (1984). The behaviour of the rare earth elements during mixing of river and sea waters. *Geochimica et Cosmochimica Acta*, 48(1), 143–149. [https://doi.org/10.1016/0016-7037\(84\)90356-9](https://doi.org/10.1016/0016-7037(84)90356-9)
- Hu, Z., Haneklaus, S., Sparovek, G., & Schnug, E. (2006). Rare earth elements in soils. *Communications in Soil Science and Plant Analysis*, 37(9–10), 1381–1420. <https://doi.org/10.1080/00103620600628680>
- Huang, Y., Colin, C., Liu, Z., Douville, E., Dapoigny, A., Haurine, F., et al. (2023). Impacts of nepheloid layers and mineralogical compositions of oceanic margin sediments on REE concentrations and Nd isotopic compositions of seawater. *Geochimica et Cosmochimica Acta*, 359, 57–70. <https://doi.org/10.1016/j.gca.2023.08.026>
- Huang, Z. Y., Wu, C. Y., & Hseu, Z. Y. (2023). Rare earth elements in tea garden soils and their bioavailability to tea buds in Taiwan. *Science of the Total Environment*, 893, 164895. <https://doi.org/10.1016/j.scitotenv.2023.164895>
- Huettel, M., Ziebis, W., Forster, S., & Luther, G. W. (1998). Advective Transport Affecting Metal and Nutrient Distributions and Interfacial Fluxes in Permeable Sediments. *Geochimica et Cosmochimica Acta*, 62(4), 613–631. [https://doi.org/10.1016/S0016-7037\(97\)00371-2](https://doi.org/10.1016/S0016-7037(97)00371-2)
- Idée, J. M., Port, M., Raynal, I., Schaefer, M., Le Greneur, S., & Corot, C. (2006). Clinical and biological consequences of transmetallation induced by contrast agents for magnetic resonance imaging: A review. *Fundamental & Clinical Pharmacology*, 20(6), 563–576. <https://doi.org/10.1111/j.1472-8206.2006.00447.x>
- Ijiri, A., Okamura, K., Ohta, J., Nishio, Y., Hamada, Y., Iijima, K., & Inagaki, F. (2018). Uptake of porewater phosphate by REY-rich mud in the western North Pacific Ocean. *Geochemical Journal*, 52(4), 373–387. <https://doi.org/10.2343/geochemj.2.0522>
- Ingrí, J., Widerlund, A., Land, M., Gustafsson, Ö., Andersson, P., & Öhlander, B. (2000). Temporal variations in the fractionation of the rare earth elements in a Boreal river: the role of colloidal particles. *Chemical Geology*, 166(1–2), 23–45. [https://doi.org/10.1016/S0009-2541\(99\)00178-3](https://doi.org/10.1016/S0009-2541(99)00178-3)
- Işıldar, A., Rene, E. R., van Hullebusch, E. D., & Lens, P. N. L. (2018). Electronic waste as a secondary source of critical metals: Management and recovery technologies. *Resources, Conservation and Recycling*, 135(December 2016), 296–312. <https://doi.org/10.1016/j.resconrec.2017.07.031>
- Jacobsen, S. B., & Wasserburg, G. J. (1980). Sm-Nd isotopic evolution of chondrites. *Earth and Planetary Science Letters*, 50(1), 139–155. [https://doi.org/10.1016/0012-821X\(80\)90125-9](https://doi.org/10.1016/0012-821X(80)90125-9)
- Jeandel, C. (1993). Concentration and isotopic composition of Nd in the South Atlantic Ocean. *Earth and Planetary Science Letters*, 117(3–4), 581–591. [https://doi.org/10.1016/0012-821X\(93\)90104-H](https://doi.org/10.1016/0012-821X(93)90104-H)
- Jeandel, C., Bishop, J., & Zindler, A. (1995). Exchange of neodymium and its isotopes between seawater and small and large particles in the Sargasso Sea. *Geochimica et Cosmochimica Acta*, 59(3), 535–547. [https://doi.org/10.1016/0016-7037\(94\)00367-U](https://doi.org/10.1016/0016-7037(94)00367-U)
- Jeandel, C., Delattre, H., Grenier, M., Pradoux, C., & Lacan, F. (2013). Rare earth element concentrations and Nd isotopes in the Southeast Pacific Ocean. *Geochemistry, Geophysics, Geosystems*, 14(2), 328–341. <https://doi.org/10.1029/2012GC004309>
- Jeandel, C., & Oelkers, E. H. (2015). The influence of terrigenous particulate material dissolution on ocean chemistry and global element cycles. *Chemical Geology*, 395, 50–66. <https://doi.org/10.1016/j.chemgeo.2014.12.001>
- Jeandel, C., & Peng, T. (1989). Isotopic composition of Nd in Atlantic surface water may signal water flow from the Pacific and Indian Oceans. *Transactions - American Geophysical Union*, 70(1132). <https://doi.org/10.1029/2001GB001635>
- Jeandel, C., Thouron, D., & Fieux, M. (1998). Concentrations and isotopic compositions of neodymium in the eastern Indian Ocean and Indonesian straits. *Geochimica et Cosmochimica Acta*, 62(15), 2597–2607. [https://doi.org/10.1016/S0016-7037\(98\)00169-0](https://doi.org/10.1016/S0016-7037(98)00169-0)
- Jensen, M., & Choppin, G. (1996). Complexation of europium(III) by aqueous orthosilicic acid. *Radiochimica Acta*, 72, 143–1150. <https://doi.org/10.1524/ract.1996.72.3.143>
- Jensen, M. P. (1994). *Competitive complexation Studies of Europium(III) and Uranium(VI) Complexation by aqueous orthosilicic acid*, College of Arts and Sciences (p. 198). Florida State University.
- Jiang, S. Y., Zhao, H. X., Chen, Y. Q., Yang, T., Yang, J. H., & Ling, H. F. (2007). Trace and rare earth element geochemistry of phosphate nodules from the lower Cambrian black shale sequence in the Mufu Mountain of Nanjing, Jiangsu province, China. *Chemical Geology*, 244(3–4), 584–604. <https://doi.org/10.1016/j.chemgeo.2007.07.010>
- Jin, P., Zhang, J., Wan, J., Overmans, S., Gao, G., Ye, M., et al. (2021). The Combined Effects of Ocean Acidification and Heavy Metals on Marine Organisms: A Meta-Analysis. *Frontiers in Marine Science*, 8, 1–14. <https://doi.org/10.3389/fmars.2021.801889>
- Johannesson, K. H., & Burdige, D. J. (2007). Balancing the global oceanic neodymium budget: Evaluating the role of groundwater. *Earth and Planetary Science Letters*, 253(1–2), 129–142. <https://doi.org/10.1016/j.epsl.2006.10.021>
- Johannesson, K. H., Chevis, D. A., Burdige, D. J., Cable, J. E., Martin, J. B., & Roy, M. (2011). Submarine groundwater discharge is an important net source of light and middle REEs to coastal waters of the Indian River Lagoon, Florida, USA. *Geochimica et Cosmochimica Acta*, 75(3), 825–843. <https://doi.org/10.1016/j.gca.2010.11.005>
- Johannesson, K. H., Cortés, A., Ramos Leal, J. A., Ramírez, A. G., & Durazo, J. (2005). Geochemistry of rare earth elements in groundwaters from a rhyolite aquifer, central México. *Rare earth elements in groundwater flow systems*, 187–222. [https://doi.org/10.1007/1-4020-3234-X\\_8](https://doi.org/10.1007/1-4020-3234-X_8)
- Johannesson, K. H., Farnham, I. M., Guo, C., & Stetzenbach, K. J. (1999). Rare earth element fractionation and concentration variations along a groundwater flow path within a shallow, basin-fill aquifer, southern Nevada, USA. *Geochimica et Cosmochimica Acta*, 63(18), 2697–2708. [https://doi.org/10.1016/S0016-7037\(99\)00184-2](https://doi.org/10.1016/S0016-7037(99)00184-2)
- Johannesson, K. H., Hawkins, D. L., & Cortés, A. (2006). Do Archean chemical sediments record ancient seawater rare earth element patterns? *Geochimica et Cosmochimica Acta*, 70(4), 871–890. <https://doi.org/10.1016/j.gca.2005.10.013>
- Johannesson, K. H., & Hendry, M. J. (2000). Rare earth element geochemistry of groundwaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochimica et Cosmochimica Acta*, 64(9), 1493–1509. [https://doi.org/10.1016/S0016-7037\(99\)00402-0](https://doi.org/10.1016/S0016-7037(99)00402-0)
- Johannesson, K. H., Lyons, W., & Bird, D. (1994). Rare earth element concentrations and speciation in alkaline lakes from the western U.S.A. *Geophysical Research Letters*, 21(9), 773–776. <https://doi.org/10.1029/94GL00005>
- Johannesson, K. H., & Lyons, W. B. (1995). Rare-earth element geochemistry of Colour Lake, an acidic freshwater lake on Axel Heiberg Island, Northwest Territories, Canada. *Chemical Geology*, 119(1–4), 209–223. [https://doi.org/10.1016/0009-2541\(94\)00099-T](https://doi.org/10.1016/0009-2541(94)00099-T)
- Johannesson, K. H., Lyons, W. B., Yelken, M. A., Gaudette, H. E., & Stetzenbach, K. J. (1996). Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: Complexation behavior and middle rare-earth element enrichments. *Chemical Geology*, 133(1–4), 125–144. [https://doi.org/10.1016/S0009-2541\(96\)00072-1](https://doi.org/10.1016/S0009-2541(96)00072-1)
- Johannesson, K. H., & Lyons, W. J. (1994). The rare earth element geochemistry of Mono Lake water and the importance of carbonate complexing. *Limnology & Oceanography*, 39(5), 1141–1154. <https://doi.org/10.4319/lo.1994.39.5.1141>
- Johannesson, K. H., Palmore, C. D., Fackrell, J., Prouty, N. G., Swarzenski, P. W., Chevis, D. A., et al. (2017). Rare earth element behavior during groundwater–seawater mixing along the Kona Coast of Hawaii. *Geochimica et Cosmochimica Acta*, 198, 229–258. <https://doi.org/10.1016/j.gca.2016.11.009>
- Johannesson, K. H., Stetzenbach, K. J., & Hodge, V. F. (1997). Rare earth elements as geochemical tracers of regional groundwater mixing. *Geochimica et Cosmochimica Acta*, 61(17), 3605–3618. [https://doi.org/10.1016/S0016-7037\(97\)00177-4](https://doi.org/10.1016/S0016-7037(97)00177-4)

- Johannesson, K. H., Stetzenbach, K. J., Hodge, V. F., Kreamer, D. K., & Zhou, X. (1997). Delineation of groundwater flow systems in the southern Great Basin using aqueous rare earth element distributions. *Ground Water*, 35(5), 807–819. <https://doi.org/10.1111/j.1745-6584.1997.tb00149.x>
- Johannesson, K. H., Stetzenbach, K. J., Hodge, V. F., & Lyons, W. B. (1996). Rare earth element complexation behavior in circumneutral pH groundwaters: Assessing the role of carbonate and phosphate ions. *Earth and Planetary Science Letters*, 139, 305–319. [https://doi.org/10.1016/0012-821X\(96\)00016-7](https://doi.org/10.1016/0012-821X(96)00016-7)
- Johannesson, K. H., Telfeyan, K., Chevis, D. A., Rosenheim, B. E., & Leybourne, M. (2014). Rare earth elements in stromatolites—1. Evidence that modern terrestrial stromatolites fractionate rare earth elements during incorporation from ambient waters. *Evolution of Archean Crust and Early Life*, 385–411. [https://doi.org/10.1007/978-94-007-7615-9\\_14](https://doi.org/10.1007/978-94-007-7615-9_14)
- Johannesson, K. H., & Zhou, X. (1999). Origin of middle rare earth element enrichments in acid waters of a Canadian High Arctic lake. *Geochimica et Cosmochimica Acta*, 63(1), 153–165. [https://doi.org/10.1016/S0016-7037\(98\)00291-9](https://doi.org/10.1016/S0016-7037(98)00291-9)
- Johannesson, K. H., Zhou, X., Guo, C., Stetzenbach, K. J., & Hodge, V. F. (2000). Origin of rare earth element signatures in groundwaters of circumneutral pH from southern Nevada and eastern California, USA. *Chemical Geology*, 164(3–4), 239–257. [https://doi.org/10.1016/S0009-2541\(99\)00152-7](https://doi.org/10.1016/S0009-2541(99)00152-7)
- Jones, C. E., Halliday, A. N., Rea, D. K., & Owen, R. M. (1994). Neodymium isotopic variations in North Pacific modern silicate sediment and the insignificance of detrital REE contributions to seawater. *Earth and Planetary Science Letters*, 127(1–4), 55–66. [https://doi.org/10.1016/0012-821X\(94\)90197-X](https://doi.org/10.1016/0012-821X(94)90197-X)
- Kamber, B. S., Greig, A., & Collerson, K. D. (2005). A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. *Geochimica et Cosmochimica Acta*, 69(4), 1041–1058. <https://doi.org/10.1016/j.gca.2004.08.020>
- Kato, Y., Fujinaga, K., Nakamura, K., Takaya, Y., Kitamura, K., Ohta, J., et al. (2011). Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. *Nature Geoscience*, 4(8), 535–539. <https://doi.org/10.1038/ngeo1185>
- Kawabe, I. (1992). Lanthanide tetrad effect in the Ln<sub>3+</sub> ionic radii and refined spin-pairing energy theory. *Geochemical Journal*, 26(6), 309–335. <https://doi.org/10.2343/geochemj.26.309>
- Kawabe, I., Toriumi, T., Ohta, A., & Miura, N. (1998). Monoisotopic REE abundances in seawater and the origin of seawater tetrad effect. *Geochemical Journal*, 32(4), 213–229. <https://doi.org/10.2343/geochemj.32.213>
- Keltjens, J., Pol, A., Reimann, J., & Op den Camp, H. (2014). PQQ-dependent methanol dehydrogenases: Rare-earth elements make a difference. *Applied Microbiology and Biotechnology*, 98(14), 6163–6183. <https://doi.org/10.1007/s00253-014-5766-8>
- Khan, A. M., Bakar, N. K. A., Bakar, A. F. A., & Ashraf, M. A. (2017). Chemical speciation and bioavailability of rare earth elements (REEs) in the ecosystem: A review. *Environmental Science and Pollution Research*, 24(29), 22764–22789. <https://doi.org/10.1007/s11356-016-7427-1>
- Kim, I., & Kim, G. (2011). Large fluxes of rare earth elements through submarine groundwater discharge (SGD) from a volcanic island, Jeju, Korea. *Marine Chemistry*, 127(1–4), 12–19. <https://doi.org/10.1016/j.marchem.2011.07.006>
- Kim, I., & Kim, G. (2014). Submarine groundwater discharge as a main source of rare earth elements in coastal waters. *Marine Chemistry*, 160, 11–17. <https://doi.org/10.1016/j.marchem.2014.01.003>
- Kim, J., Torres, M. E., Haley, B. A., Kastner, M., Pohlman, J. W., Riedel, M., & Lee, Y. (2012). The effect of diagenesis and fluid migration on rare earth element distribution in pore fluids of the northern Cascadia accretionary margin. *Chemical Geology*, 291, 152–165. <https://doi.org/10.1016/j.chemgeo.2011.10.010>
- Kim, J. H., Torres, M. E., Haley, B. A., Ryu, J. S., Park, M. H., Hong, W. L., & Choi, J. (2016). Marine silicate weathering in the anoxic sediment of the Ulleung Basin: Evidence and consequences. *Geochemistry, Geophysics, Geosystems*, 17(8), 3437–3453. <https://doi.org/10.1002/2016GC006356>
- Kim, T., Kim, H., & Kim, G. (2020). Tracing river water versus wastewater sources of trace elements using rare earth elements in the Nakdong River estuarine waters. *Marine Pollution Bulletin*, 160, 111589. <https://doi.org/10.1016/j.marpolbul.2020.111589>
- Klinkhammer, G. (1980). Early diagenesis in sediments from the eastern equatorial Pacific, II. Pore water metal results. *Earth and Planetary Science Letters*, 49(1), 81–101. [https://doi.org/10.1016/0012-821X\(80\)90151-X](https://doi.org/10.1016/0012-821X(80)90151-X)
- Klinkhammer, G., Elderfield, H., & Hudson, A. (1983). Rare earth elements in seawater near hydrothermal vents. *Nature*, 305(5931), 185–188. <https://doi.org/10.1038/305185a0>
- Klinkhammer, G., German, C. R., Elderfield, H., Greaves, M. J., & Mitra, A. (1994). Rare earth elements in hydrothermal fluids and plume particulates by inductively coupled plasma mass spectrometry. *Marine Chemistry*, 45(3), 179–186. [https://doi.org/10.1016/0304-4203\(94\)90001-9](https://doi.org/10.1016/0304-4203(94)90001-9)
- Koepfenkastro, D., & De Carlo, E. H. (1992). Sorption of rare-earth elements from seawater onto synthetic mineral particles: An experimental approach. *Chemical Geology*, 95(3–4), 251–263. [https://doi.org/10.1016/0009-2541\(92\)90015-W](https://doi.org/10.1016/0009-2541(92)90015-W)
- Koepfenkastro, D., & De Carlo, E. H. (1993). Uptake of Rare Earth Elements from Solution by Metal Oxides. *Environmental Science and Technology*, 27(9), 1796–1802. <https://doi.org/10.1021/es00046a006>
- Koepfenkastro, D., Decarlo, E. H., & Roth, M. (1991). A method to investigate the interaction of rare earth elements in aqueous solution with metal oxides. *Journal of Radioanalytical and Nuclear Chemistry*, 152(2), 337–346. <https://doi.org/10.1007/BF02104687>
- Komar, D., Rogan Šmuc, N., Lambaša Belak, Ž., Slavica Matešić, S., Lojen, S., Kniewald, G., et al. (2014). Geochemical Characteristics and Distribution of Rare Earth Elements in Makirina Bay Sediments (N. Dalmatia, Republic of Croatia). *Geologica Macedonica*, 28(2), 127–137.
- Kotelnikova, A. D., Rogova, O. B., & Stolbova, V. V. (2021). Lanthanides in the Soil: Routes of Entry, Content, Effect on Plants, and Genotoxicity (a Review). *Eurasian Soil Science*, 54(1), 117–134. <https://doi.org/10.1134/S1064229321010051>
- Kraemer, D., & Bau, M. (2022). Siderophores and the formation of cerium anomalies in anoxic environments. *Geochemical Perspectives Letters*, 22, 50–55. <https://doi.org/10.7185/geochemlet.2227>
- Kreamer, D. K., Hodge, V. F., Rabinowitz, I., Johannesson, K. H., & Stetzenbach, K. J. (1996). Trace Element Geochemistry in Water from Selected Springs in Death Valley National Park, California. *Ground Water*, 34(1), 95–103. <https://doi.org/10.1111/j.1745-6584.1996.tb01869.x>
- Kulaksiz, S., & Bau, M. (2007). Contrasting behaviour of anthropogenic gadolinium and natural rare earth elements in estuaries and the gadolinium input into the North Sea. *Earth and Planetary Science Letters*, 260(1–2), 361–371. <https://doi.org/10.1016/j.epsl.2007.06.016>
- Kulaksiz, S., & Bau, M. (2011). Anthropogenic gadolinium as a microcontaminant in tap water used as drinking water in urban areas and megacities. *Applied Geochemistry*, 26(11), 1877–1885. <https://doi.org/10.1016/j.apgeochem.2011.06.011>
- Kulaksiz, S., & Bau, M. (2013). Anthropogenic dissolved and colloid/nanoparticle-bound samarium, lanthanum and gadolinium in the Rhine River and the impending destruction of the natural rare earth element distribution in rivers. *Earth and Planetary Science Letters*, 362, 43–50. <https://doi.org/10.1016/j.epsl.2012.11.033>
- Kumar, K., Saion, E., Halimah, M. K., Ck, Y., & Hamzah, M. S. (2014). Rare earth element (REE) in surface mangrove sediment by instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 301(3), 667–676. <https://doi.org/10.1007/s10967-014-3221-z>

- Kuss, J., Garbe-Schönberg, C. D., & Kremling, K. (2001). Rare earth elements in suspended particulate material of North Atlantic surface waters. *Geochimica et Cosmochimica Acta*, 65(2), 187–199. [https://doi.org/10.1016/S0016-7037\(00\)00518-4](https://doi.org/10.1016/S0016-7037(00)00518-4)
- Lacan, F., & Jeandel, C. (2001). Tracing Papua New Guinea imprint on the central Equatorial Pacific Ocean using neodymium isotopic compositions and Rare Earth Element patterns. *Earth and Planetary Science Letters*, 186(3–4), 497–512. [https://doi.org/10.1016/S0012-821X\(01\)00263-1](https://doi.org/10.1016/S0012-821X(01)00263-1)
- Lacan, F., & Jeandel, C. (2004). Denmark Strait water circulation traced by heterogeneity in neodymium isotopic compositions. *Deep-Sea Research Part I Oceanographic Research Papers*, 51(1), 71–82. <https://doi.org/10.1016/j.dsr.2003.09.006>
- Lacan, F., & Jeandel, C. (2005). Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent – Ocean interface. *Earth and Planetary Science Letters*, 232(3–4), 245–257. <https://doi.org/10.1016/j.epsl.2005.01.004>
- Lachaux, N., Cossu-Leguille, C., Poirier, L., Gross, E. M., & Giamberini, L. (2022). Integrated environmental risk assessment of rare earth elements mixture on aquatic ecosystems. *Frontiers in Environmental Science*, 10(September). <https://doi.org/10.3389/fenvs.2022.974191>
- Laczniak, R. J., Cole, J. C., Sawyer, D. A., & Trudeau, D. A. (1996). *Summary of hydrogeological controls on ground-water flow at the Nevada test site, Nye county, Nevada*. U. S. Geol. Surv. Water Resour. Investigations Report.
- Ladonin, D. V. (2017). Lanthanides in soils of the Cherepovets steel mill impact zone. *Eurasian Soil Science*, 50(6), 672–680. <https://doi.org/10.1134/S1064229317060047>
- Lagarde, M., Lemaitre, N., Planquette, H., Grenier, M., Belhadj, M., Lherminier, P., & Jeandel, C. (2020). Particulate rare earth element behavior in the North Atlantic (GEOVIDE cruise). *Biogeosciences*, 17(22), 5539–5561. <https://doi.org/10.5194/bg-17-5539-2020>
- Lai, J., Liu, J., Wu, D., & Xu, J. (2023). Pollution and health risk assessment of rare earth elements in Citrus sinensis growing soil in mining area of southern China. *PeerJ*, 11, e15470. <https://doi.org/10.7717/peerj.15470>
- Lambelet, M., van de Flierdt, T., Crockett, K., Rehkämper, M., Kreissig, K., Coles, B., et al. (2016). Neodymium isotopic composition and concentration in the western North Atlantic Ocean: Results from the GEOTRACES GA02 section. *Geochimica et Cosmochimica Acta*, 177, 1–29. <https://doi.org/10.1016/j.gca.2015.12.019>
- Lawrence, M. G., & Kamber, B. S. (2006). The behaviour of the rare earth elements during estuarine mixing-revisited. *Marine Chemistry*, 100(1–2), 147–161. <https://doi.org/10.1016/j.marchem.2005.11.007>
- Lecomte, K. L., Sarmiento, A. M., Borrego, J., & Nieto, J. M. (2017). Rare earth elements mobility processes in an AMD-affected estuary: Huelva Estuary (SW Spain). *Marine Pollution Bulletin*, 121(1–2), 282–291. <https://doi.org/10.1016/j.marpolbul.2017.06.030>
- Lee, J. H., & Byrne, R. H. (1994). Pressure dependence of gadolinium carbonate complexation in seawater. *Geochimica et Cosmochimica Acta*, 58(19), 4009–4016. [https://doi.org/10.1016/0016-7037\(94\)90263-1](https://doi.org/10.1016/0016-7037(94)90263-1)
- Leite, C., Coppola, F., Monteiro, R., Russo, T., Polese, G., Silva, M. R. F., et al. (2020). Toxic impacts of rutile titanium dioxide in *Mytilus galloprovincialis* exposed to warming conditions. *Chemosphere*, 252, 126563. <https://doi.org/10.1016/j.chemosphere.2020.126563>
- Leite, C., Coppola, F., Queirós, V., Russo, T., Gianluca, P., Pretti, C., et al. (2023). Can temperature influence the impacts in *Mytilus galloprovincialis* by neodymium? Comparison between exposure and recovery periods. *Environmental Toxicology and Pharmacology*, 97, 104029. <https://doi.org/10.1016/j.etap.2022.104029>
- Leite, C., Russo, T., Cuccaro, A., Pinto, J., Polese, G., Soares, A. M. V. M., et al. (2024). Praseodymium and warming interactions in mussels: Comparison between observed and predicted results. *Science of the Total Environment*, 29(April 2024), 172893. <https://doi.org/10.1016/j.scitotenv.2024.172893>
- Leong, J. A. M., & Shock, E. L. (2020). Thermodynamic constraints on the geochemistry of low-temperature, continental, serpentinization-generated fluids. *American Journal of Science*, 320(3), 185–325. <https://doi.org/10.2475/03.2020.01>
- Lerat-Hardy, A., Coynel, A., Dutruch, L., Pereto, C., Bossy, C., Gil-Diaz, T., et al. (2019). Rare Earth Element fluxes over 15 years into a major European Estuary (Garonne-Gironde, SW France): Hospital effluents as a source of increasing gadolinium anomalies. *Science of the Total Environment*, 656, 409–420. <https://doi.org/10.1016/j.scitotenv.2018.11.343>
- Liang, C., & Shen, J. (2022). Removal of yttrium from rare-earth wastewater by *Serratia marcescens*: Biosorption optimization and mechanisms studies. *Scientific Reports*, 12(1), 1–14. <https://doi.org/10.1038/s41598-022-08542-0>
- Lide, D. R., & Haynes, W. M. (2009). *Handbook of chemistry and physics* (90th ed.). CRC Press.
- Lima, A. T., & Ottosen, L. (2021). Recovering rare earth elements from contaminated soils: Critical overview of current remediation technologies. *Chemosphere*, 265, 129163. <https://doi.org/10.1016/j.chemosphere.2020.129163>
- Lin, Y. T., Liu, R. X., Audira, G., Suryanto, M., Roldan, M., Lee, J.-S., et al. (2022). Lanthanides Toxicity in Zebrafish Embryos Are Correlated to Their Atomic Number. *Toxics*, 10(6), 336–350. <https://doi.org/10.3390/toxics10060336>
- Liu, W. S., Guo, M. N., Liu, C., Yuan, M., Chen, X. T., Huot, H., et al. (2019a). Water, sediment and agricultural soil contamination from an ion-adsorption rare earth mining area. *Chemosphere*, 216, 75–83. <https://doi.org/10.1016/j.chemosphere.2018.10.109>
- Liu, X., Hardisty, D. S., Lyons, T. W., & Swart, P. K. (2019). Evaluating the fidelity of the cerium paleoredox tracer during variable carbonate diagenesis on the Great Bahamas Bank. *Geochimica et Cosmochimica Acta*, 248, 25–42. <https://doi.org/10.1016/j.gca.2018.12.028>
- Liu, Y., Wu, M., Zhang, L., Bi, J., Song, L., Wang, L., et al. (2019). Prenatal exposure of rare earth elements cerium and ytterbium and neonatal thyroid stimulating hormone levels: Findings from a birth cohort study. *Environment International*, 133(September), 105222. <https://doi.org/10.1016/j.envint.2019.105222>
- Liu, Y., Wu, Q., Jia, H., Wang, Z., Gao, S., & Zeng, J. (2022). Anthropogenic rare earth elements in urban lakes: Their spatial distributions and tracing application. *Chemosphere*, 300(November 2021), 134534. <https://doi.org/10.1016/j.chemosphere.2022.134534>
- López-González, N., Borrego, J., Carro, B., Grande, J. A., de la Torre, M. L., & Valente, T. (2012). Rare-earth-element fractionation patterns in estuarine sediments as a consequence of acid mine drainage: A case study in SW Spain. *Boletín Geológico y Minero*, 123(1), 55–64.
- Lovley, D. R., & Chapelle, F. H. (1995). Deep subsurface microbial processes. *Reviews of Geophysics*, 33(3), 365–381. <https://doi.org/10.1029/95RG01305>
- Lumiste, K., Mänd, K., Bailey, J., Paiste, P., Lang, L., Lepland, A., & Kirsimäe, K. (2019). REE+Y uptake and diagenesis in Recent sedimentary apatites. *Chemical Geology*, 525(May), 268–281. <https://doi.org/10.1016/j.chemgeo.2019.07.034>
- Luoma, S. N. (1983). Bioavailability of trace metals to aquatic organisms—A review. *Science of the Total Environment*, 28(1–3), 1–22. [https://doi.org/10.1016/S0048-9697\(83\)80004-7](https://doi.org/10.1016/S0048-9697(83)80004-7)
- Luoma, S. N. (1989). Can we determine the biological availability of sediment-bound trace elements? *Hydrobiologia*, 176(1), 379–396. <https://doi.org/10.1007/BF00026572>
- Lyons, W., Tyler, S., Gaudette, H., & Long, D. (1995). The use of strontium isotopes in determining groundwater mixing and brine fingering in a playa spring zone, Lake Tyrrell, Australia. *Journal of Hydrology*, 167(1–4), 225–239. [https://doi.org/10.1016/0022-1694\(94\)02601-7](https://doi.org/10.1016/0022-1694(94)02601-7)
- Ma, L., Dang, D. H., Wang, W., Evans, R. D., & Wang, W. X. (2019). Rare earth elements in the Pearl River Delta of China: Potential impacts of the REE industry on water, suspended particles and oysters. *Environmental Pollution*, 244, 190–201. <https://doi.org/10.1016/j.envpol.2018.10.015>

- Ma, L., & Wang, W. (2023). Dissolved rare earth elements in the Pearl River Delta: Using Gd as a tracer of anthropogenic activity from river towards the sea. *Science of the Total Environment*, 856(May 2022), 159241. <https://doi.org/10.1016/j.scitotenv.2022.159241>
- Ma, Y., Wang, J., Peng, C., Ding, Y., He, X., Zhang, P., et al. (2016). Toxicity of cerium and thorium on *Daphnia magna*. *Ecotoxicology and Environmental Safety*, 134, 226–232. <https://doi.org/10.1016/j.ecoenv.2016.09.006>
- MacLeod, K. G., & Irving, A. J. (1996). Correlation of cerium anomalies with indicators of paleoenvironment. *Journal of Sedimentary Research*, 66(5), 948–955. <https://doi.org/10.1306/D426844B-2B26-11D7-8648000102C1865D>
- MacMillan, G. A., Chételat, J., Heath, J. P., Mickpegak, R., & Amyot, M. (2017). Rare earth elements in freshwater, marine, and terrestrial ecosystems in the eastern Canadian Arctic. *Environmental Sciences: Processes & Impacts*, 19(10), 1336–1345. <https://doi.org/10.1039/c7em00082k>
- Macmillan, G. A., Clayden, M. G., Chételat, J., Richardson, M. C., Ponton, D. E., Perron, T., & Amyot, M. (2019). Environmental Drivers of Rare Earth Element Bioaccumulation in Freshwater Zooplankton. *Environmental Science and Technology*, 53(3), 1650–1660. <https://doi.org/10.1021/acs.est.8b05547>
- Mandal, S. K., Ray, R., González, A. G., Mavromatis, V., Pokrovsky, O. S., & Jana, T. K. (2019). State of rare earth elements in the sediment and their bioaccumulation by mangroves: A case study in pristine islands of Indian Sundarban. *Environmental Science and Pollution Research*, 26(9), 9146–9160. <https://doi.org/10.1007/s11356-019-04222-1>
- Marginson, H., MacMillan, G. A., Grant, E., Gérin-Lajoie, J., & Amyot, M. (2023). Rare earth element bioaccumulation and cerium anomalies in biota from the Eastern Canadian subarctic (Nunavik). *Science of the Total Environment*, 879, 163024. <https://doi.org/10.1016/j.scitotenv.2023.163024>
- Marsac, R., Catrouillet, C., Davranche, M., Bouhnik-Le Coz, M., Briant, N., Janot, N., et al. (2021). Modeling rare earth elements binding to humic acids with model VII. *Chemical Geology*, 567, 120099. <https://doi.org/10.1016/j.chemgeo.2021.120099>
- Marsac, R., Davranche, M., Gruau, G., Bouhnik-Le Coz, M., & Dia, A. (2011). An improved description of the interactions between rare earth elements and humic acids by modeling: PHREEQC-Model VI coupling. *Geochimica et Cosmochimica Acta*, 75(19), 5625–5637. <https://doi.org/10.1016/j.gca.2011.07.009>
- Marsac, R., Davranche, M., Gruau, G., & Dia, A. (2010). Metal loading effect on rare earth element binding to humic acid: Experimental and modelling evidence. *Geochimica et Cosmochimica Acta*, 74(6), 1749–1761. <https://doi.org/10.1016/j.gca.2009.12.006>
- Martin, E., & Haley, B. A. (2000). Fossil fish teeth as proxies for seawater Sr and Nd isotopes. *Geochimica et Cosmochimica Acta*, 64(5), 835–847. [https://doi.org/10.1016/S0016-7037\(99\)00376-2](https://doi.org/10.1016/S0016-7037(99)00376-2)
- Martin, E., Macdougall, J., Herbert, T., Paytan, A., & Kastner, M. (1995). Strontium and neodymium isotopic analyses of marine barite separates. *Geochimica et Cosmochimica Acta*, 59(7), 1353–1361. [https://doi.org/10.1016/0016-7037\(95\)00049-6](https://doi.org/10.1016/0016-7037(95)00049-6)
- Massari, S., & Ruberti, M. (2013). Rare earth elements as critical raw materials: Focus on international markets and future strategies. *Resources Policy*, 38(1), 36–43. <https://doi.org/10.1016/j.resourpol.2012.07.001>
- Masuda, A. (1962). Regularities in variation of relative abundances of lanthanide elements and an attempt to analyse separation-index patterns of some minerals. *Journal of Earth Sciences*, 10, 173–187.
- Masuda, A. (1975). Abundances of monoisotopic REE, consistent with the Leedy chondrite values. *Geochemical Journal*, 9(3), 183–184. <https://doi.org/10.2343/geochemj.9.183>
- Maulvault, A. L., Camacho, C., Barbosa, V., Alves, R., Anacleto, P., Fogaça, F., et al. (2018). Assessing the effects of seawater temperature and pH on the bioaccumulation of emerging chemical contaminants in marine bivalves. *Environmental Research*, 161(July 2017), 236–247. <https://doi.org/10.1016/j.envres.2017.11.017>
- McCarthy, J. F., Stafford, P. L., & Toran, L. E. (1996). Colloid-facilitated field-scale transport of lanthanides and actinides in fractured saprolite. *Eos*, 77, F212.
- McDonough, W. F., & Sun, S. s. (1995). The composition of the Earth. *Chemical Geology*, 120(3–4), 223–253. [https://doi.org/10.1016/0009-2541\(94\)00140-4](https://doi.org/10.1016/0009-2541(94)00140-4)
- McLennan, S. M. (1989). Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. In B. Lipin & G. McKay (Eds.), *Geochemistry and mineralogy of rare Earth elements, Reviews in mineralogy* (pp. 169–200).
- McLennan, S. M. (1994). Rare earth element geochemistry and the “tetrad” effect. *Geochimica et Cosmochimica Acta*, 58(9), 2025–2033. <https://doi.org/10.1007/s11004-021-09959-5>
- Merschel, G., & Bau, M. (2015). Rare earth elements in the aragonitic shell of freshwater mussel *Corbicula fluminea* and the bioavailability of anthropogenic lanthanum, samarium and gadolinium in river water. *Science of the Total Environment*, 533, 91–101. <https://doi.org/10.1016/j.scitotenv.2015.06.042>
- Merschel, G., Bau, M., Baldewein, L., Dantas, E. L., Walde, D., & Bühn, B. (2015). Tracing and tracking wastewater-derived substances in freshwater lakes and reservoirs: Anthropogenic gadolinium and geogenic REEs in Lake Paranoá, Brasília. *Comptes Rendus Geoscience*, 347(5–6), 284–293. <https://doi.org/10.1016/j.crte.2015.01.004>
- Merschel, G., Bau, M., & Dantas, E. L. (2017). Contrasting impact of organic and inorganic nanoparticles and colloids on the behavior of particle-reactive elements in tropical estuaries: An experimental study. *Geochimica et Cosmochimica Acta*, 197, 1–13. <https://doi.org/10.1016/j.gca.2016.09.041>
- Meyer, A. C. S., Grundle, D., & Cullen, J. T. (2021). Selective uptake of rare earth elements in marine systems as an indicator of and control on aerobic bacterial methanotrophy. *Earth and Planetary Science Letters*, 558, 116756. <https://doi.org/10.1016/j.epsl.2021.116756>
- Michard, A. (1989). Rare earth element systematics in hydrothermal fluids. *Geochimica et Cosmochimica Acta*, 53(3), 745–750. [https://doi.org/10.1016/0016-7037\(89\)90017-3](https://doi.org/10.1016/0016-7037(89)90017-3)
- Migdisov, A. A., & Williams-Jones, A. E. (2006). A spectrophotometric study of erbium (III) speciation in chloride solutions at elevated temperatures. *Chemical Geology*, 234(1–2), 17–27. <https://doi.org/10.1016/j.chemgeo.2006.04.002>
- Migdisov, A. A., & Williams-Jones, A. E. (2007). An experimental study of the solubility and speciation of neodymium (III) fluoride in F-bearing aqueous solutions. *Geochimica et Cosmochimica Acta*, 71(12), 3056–3069. <https://doi.org/10.1016/j.gca.2007.04.004>
- Migdisov, A. A., Williams-Jones, A. E., Normand, C., & Wood, S. A. (2008). A spectrophotometric study of samarium (III) speciation in chloride solutions at elevated temperatures. *Geochimica et Cosmochimica Acta*, 72(6), 1611–1625. <https://doi.org/10.1016/j.gca.2008.01.007>
- Millero, F., Woosley, R., DiTrollo, B., & Waters, J. (2009). Effect of Ocean Acidification on the Speciation of Metals in Seawater. *Oceanography*, 22(4), 72–85. <https://doi.org/10.5670/oceanog.2009.98>
- Millero, F. J. (1992). Stability constants for the formation of rare earth-inorganic complexes as a function of ionic strength. *Geochimica et Cosmochimica Acta*, 56(8), 3123–3132. [https://doi.org/10.1016/0016-7037\(92\)90293-R](https://doi.org/10.1016/0016-7037(92)90293-R)
- Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., & Tipping, E. (2003). Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environmental Science & Technology*, 37(5), 958–971. <https://doi.org/10.1021/es0258879>
- Minami, E. (1935). Gehalte an seltenen Erden in europäischen und japanischen. *Nach. Ges. Wiss. Goettingen*, 1, 155–170.

- Mirlean, N., Calliari, L., & Johannesson, K. (2020). Dredging in an estuary causes contamination by fluid mud on a tourist ocean beach. Evidence via REE ratios. *Marine Pollution Bulletin*, 159(May), 111495. <https://doi.org/10.1016/j.marpolbul.2020.111495>
- Moermond, C. T. A., Tijink, J., van Wezel, A. P., & Koelmans, A. a. (2001). Distribution, speciation, and bioavailability of lanthanides in the Rhine-Meuse estuary, The Netherlands. *Environmental Toxicology and Chemistry*, 20(9), 1916–1926. <https://doi.org/10.1002/etc.5620200909>
- Moffett, J. W. (1990). Microbially mediated cerium oxidation in sea water. *Nature*, 345(6274), 421–423. <https://doi.org/10.1038/345421a0>
- Moffett, J. W. (1994). The relationship between cerium and manganese oxidation in the marine environment. *Limnology & Oceanography*, 39(6), 1309–1318. <https://doi.org/10.4319/lo.1994.39.6.1309>
- Molina-kescher, M., Frank, M., & Hathorne, E. (2014). South Pacific dissolved Nd isotope compositions and rare earth element distributions: Water mass mixing versus biogeochemical cycling. *Geochimica et Cosmochimica Acta*, 127, 171–189. <https://doi.org/10.1016/j.gca.2013.11.038>
- Molina-Kescher, M., Hathorne, E. C., Osborne, A. H., Behrens, M. K., Kölling, M., Pahnke, K., & Frank, M. (2018). The influence of Basaltic Islands on the Oceanic REE Distribution: A case study from the tropical South Pacific. *Frontiers in Marine Science*, 5. <https://doi.org/10.3389/fmars.2018.00050>
- Möller, P., & Bau, M. (1993). Rare-earth patterns with positive cerium anomaly in alkaline waters from Lake Van, Turkey. *Earth and Planetary Science Letters*, 117(3–4), 671–676. [https://doi.org/10.1016/0012-821X\(93\)90110-U](https://doi.org/10.1016/0012-821X(93)90110-U)
- Möller, P., Paces, T., Dulski, P., & Morteani, G. (2002). Anthropogenic Gd in surface water, drainage system, and the water supply of the city of Prague, Czech Republic. *Environmental Science & Technology*, 36(11), 2387–2394. <https://doi.org/10.1021/es010235q>
- Monecke, T., Kempe, U., Monecke, J., Sala, M., & Wolf, D. (2002). Tetrad effect in rare earth element distribution patterns: A method of quantification with application to rock and mineral samples from granite-related rare metal deposits. *Geochimica et Cosmochimica Acta*, 66(7), 1185–1196. [https://doi.org/10.1016/S0016-7037\(01\)00849-3](https://doi.org/10.1016/S0016-7037(01)00849-3)
- Morad, S., & Felitsyn, S. (2001). Identification of primary Ce-anomaly signatures in fossil biogenic apatite: Implication for the Cambrian oceanic anoxia and phosphogenesis. *Sedimentary Geology*, 143(3–4), 259–264. [https://doi.org/10.1016/S0037-0738\(01\)00093-8](https://doi.org/10.1016/S0037-0738(01)00093-8)
- Morel, E., Cui, L., Zerges, W., & Wilkinson, K. J. (2021). Mixtures of rare earth elements show antagonistic interactions in *Chlamydomonas reinhardtii*. *Environmental Pollution*, 287, 117594. <https://doi.org/10.1016/j.envpol.2021.117594>
- Morel, F., & Morgan, J. (1972). A numerical method for computing equilibria in aqueous chemical systems. *Environmental Science & Technology*, 6(1), 58–67. <https://doi.org/10.1021/es60060a006>
- Morgan, B., Johnston, S. G., Burton, E. D., & Hagan, R. E. (2016). Acidic drainage drives anomalous rare earth element signatures in intertidal mangrove sediments. *Science of the Total Environment*, 573, 831–840. <https://doi.org/10.1016/j.scitotenv.2016.08.172>
- Moriwaki, H., Koide, R., Yoshikawa, R., Warabino, Y., & Yamamoto, H. (2013). Adsorption of rare earth ions onto the cell walls of wild-type and lipoteichoic acid-defective strains of *Bacillus subtilis*. *Applied Microbiology and Biotechnology*, 97(8), 3721–3728. <https://doi.org/10.1007/s00253-012-4200-3>
- Moriwaki, H., & Yamamoto, H. (2013). Interactions of microorganisms with rare earth ions and their utilization for separation and environmental technology. *Applied Microbiology and Biotechnology*, 97(1), 1–8. <https://doi.org/10.1007/s00253-012-4519-9>
- Morosetti, B., Freitas, R., Pereira, E., Hamza, H., Andrade, M., Coppola, F., et al. (2020). Will temperature rise change the biochemical alterations induced in *Mytilus galloprovincialis* by cerium oxide nanoparticles and mercury? *Environmental Research*, 188, 109778. <https://doi.org/10.1016/j.envres.2020.109778>
- Munksgaard, N. C., Lim, K., & Parry, D. L. (2003). Rare earth elements as provenance indicators in North Australian estuarine and coastal marine sediments. *Estuarine, Coastal and Shelf Science*, 57(3), 399–409. [https://doi.org/10.1016/S0272-7714\(02\)00368-2](https://doi.org/10.1016/S0272-7714(02)00368-2)
- Murray, R. W., Buchholtz ten Brink, M. R., Brumsack, H. J., Gerlach, D. C., & Russ III, G. P. (1991). Rare earth elements in Japan Sea sediments and diagenetic behavior of Ce/Ce\*: Results from ODP Leg 127. *Geochimica et Cosmochimica Acta*, 55(9), 2453–2466. [https://doi.org/10.1016/0016-7037\(91\)90365-C](https://doi.org/10.1016/0016-7037(91)90365-C)
- Nakagawa, T., Mitsui, R., Tani, A., Sasa, K., Tashiro, S., Iwama, T., et al. (2012). A Catalytic Role of XoxF1 as La3+-Dependent Methanol Dehydrogenase in *Methylobacterium extorquens* Strain AM1. *PLoS One*, 7(11), 1–7. <https://doi.org/10.1371/journal.pone.0050480>
- Nakai, S., Halliday, A., & Rea, D. (1993). Trace element abundance, and Sr and Nd isotope ratios of dust samples in the Pacific Ocean (Table 2). *Pangea*.
- Nakamura, Y., Tsumura, Y., Tonogai, Y., Shibata, T., & Ito, Y. (1997). Differences in behavior among the chlorides of seven rare earth elements administered intravenously to rats. *Fundamental and Applied Toxicology*, 37(2), 106–116. <https://doi.org/10.1006/faat.1997.2322>
- Nance, W. B., & Taylor, S. R. (1976). Rare earth element patterns and crustal sedimentary rocks. *Geochimica et Cosmochimica Acta*, 40(12), 1539–1551. [https://doi.org/10.1016/0016-7037\(76\)90093-4](https://doi.org/10.1016/0016-7037(76)90093-4)
- Nanchaiah, Y. V., Mohan, S. V., & Lens, P. N. L. (2016). Biological and Bioelectrochemical Recovery of Critical and Scarce Metals. *Trends in Biotechnology*, 34(2), 137–155. <https://doi.org/10.1016/j.tibtech.2015.11.003>
- Nesbitt, H. (1979). Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature*, 279(5710), 206–210. <https://doi.org/10.1038/279206a0>
- Nigro, A., Sappa, G., & Barbieri, M. (2018). Boron isotopes and rare earth elements in the groundwater of a landfill site. *Journal of Geochemical Exploration*, 190(September 2017), 200–206. <https://doi.org/10.1016/j.gexplo.2018.02.019>
- Nozaki, Y., & Alibo, D. S. (2003). Importance of vertical geochemical processes in controlling the oceanic profiles of dissolved rare earth elements in the northeastern Indian Ocean. *Earth and Planetary Science Letters*, 205(3–4), 155–172. [https://doi.org/10.1016/S0012-821X\(02\)01027-0](https://doi.org/10.1016/S0012-821X(02)01027-0)
- Nozaki, Y., Alibo, D. S., Amakawa, H., Gamo, T., & Hasumoto, H. (1999). Dissolved rare earth elements and hydrography in the Sulu Sea. *Geochimica et Cosmochimica Acta*, 63(15), 2171–2181. [https://doi.org/10.1016/S0016-7037\(99\)00142-8](https://doi.org/10.1016/S0016-7037(99)00142-8)
- Nozaki, Y., Lerche, D., Alibo, D. S., & Snidvongs, A. (2000). The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. *Geochimica et Cosmochimica Acta*, 64(23), 3983–3994. [https://doi.org/10.1016/S0016-7037\(00\)00473-7](https://doi.org/10.1016/S0016-7037(00)00473-7)
- Nozaki, Y., Zhang, J., & Amakawa, H. (1997). The fractionation between Y and Ho in the marine environment. *Earth and Planetary Science Letters*, 148(1–2), 329–340. [https://doi.org/10.1016/S0012-821X\(97\)00034-4](https://doi.org/10.1016/S0012-821X(97)00034-4)
- Ohnuki, T., Ozaki, T., Kozai, N., Nankawa, T., Sakamoto, F., Sakai, T., et al. (2008). Concurrent transformation of Ce(III) and formation of biogenic manganese oxides. *Chemical Geology*, 253(1–2), 23–29. <https://doi.org/10.1016/j.chemgeo.2008.03.013>
- Ohta, A., & Kawabe, I. (2001). REE (III) adsorption onto Mn dioxide (◆-MnO<sub>2</sub>) and Fe oxyhydroxide. *Geochimica et Cosmochimica Acta*, 65(5), 695–703. [https://doi.org/10.1016/S0016-7037\(00\)00578-0](https://doi.org/10.1016/S0016-7037(00)00578-0)
- Ohta, J., Yasukawa, K., Machida, S., Fujinaga, K., Nakamura, K., Takaya, Y., et al. (2016). Geological factors responsible for REY-rich mud in the western North Pacific Ocean: Implications from mineralogical and grain size distributions. *Geochemical Journal*, 50(6), 591–603. <https://doi.org/10.2343/geochemj.2.0435>

- Ojiambo, S. B., Lyons, W. B., Welch, K. A., Poreda, R. J., & Johannesson, K. H. (2003). Strontium isotopes and rare earth elements as tracers of groundwater-lake water interactions, Lake Naivasha, Kenya. *Applied Geochemistry*, 18(11), 1789–1805. [https://doi.org/10.1016/S0883-2927\(03\)00104-5](https://doi.org/10.1016/S0883-2927(03)00104-5)
- Oka, A., Tazoe, H., & Obata, H. (2021). Simulation of global distribution of rare earth elements in the ocean using an ocean general circulation model. *Journal of Oceanography*, 77(3), 413–430. <https://doi.org/10.1007/s10872-021-00600-x>
- Olivarez, A. M., & Owen, R. M. (1989). REE/Fe variations in hydrothermal sediments: Implications for the REE content of seawater. *Geochimica et Cosmochimica Acta*, 53(3), 757–762. [https://doi.org/10.1016/0016-7037\(89\)90019-7](https://doi.org/10.1016/0016-7037(89)90019-7)
- Olivarez, A. M., & Owen, R. M. (1991). The europium anomaly of seawater: Implications for fluvial versus hydrothermal REE inputs to the oceans. *Chemical Geology*, 92(4), 317–328. [https://doi.org/10.1016/0009-2541\(91\)90076-4](https://doi.org/10.1016/0009-2541(91)90076-4)
- Olmez, I., Sholkovltz, E. R., Hermann, D., & Eganhouse, R. P. (1991). Rare Earth Elements in Sediments off Southern California: A New Anthropogenic Indicator. *Environmental Science and Technology*, 25(2), 310–316. <https://doi.org/10.1021/es00014a015>
- Omonona, O. V., & Okogbue, C. O. (2017). Geochemistry of rare earth elements in groundwater from different aquifers in the Gboko area, central Benue Trough, Nigeria. *Environmental Earth Sciences*, 76(1), 1–19. <https://doi.org/10.1007/s12665-016-6329-3>
- Orani, A. M., Vassileva, E., & Thomas, O. P. (2022). Marine sponges as coastal bioindicators of rare earth elements bioaccumulation in the French Mediterranean Sea. *Environmental Pollution*, 304(March), 119172. <https://doi.org/10.1016/j.envpol.2022.119172>
- Osborne, A. H., Haley, B. A., Hathorne, E. C., Plancherel, Y., & Frank, M. (2015). Rare earth element distribution in Caribbean seawater: Continental inputs versus lateral transport of distinct REE compositions in subsurface water masses. *Marine Chemistry*, 177, 172–183. <https://doi.org/10.1016/j.marchem.2015.03.013>
- Osborne, A. H., Hathorne, E. C., Schijf, J., Plancherel, Y., Böning, P., & Frank, M. (2017). The potential of sedimentary foraminiferal rare earth element patterns to trace water masses in the past. *Geochemistry, Geophysics, Geosystems*, 18(4), 1550–1568. <https://doi.org/10.1002/2016GC006782>
- Ospina-Álvarez, N., Caetano, M., Vale, C., Santos-Echeandía, J., Bernárdez, P., & Prego, R. (2014). Exchange of nutrients across the sediment-water interface in intertidal ria systems (SW Europe). *Journal of Sea Research*, 85, 349–358. <https://doi.org/10.1016/j.seares.2013.07.002>
- Paffrath, R., Pahnke, K., Behrens, M. K., Reckhardt, A., Ehler, C., Schnetzger, B., & Brumsack, H. J. (2020). Rare Earth Element Behavior in a Sandy Subterranean Estuary of the Southern North Sea. *Frontiers in Marine Science*, 7(June). <https://doi.org/10.3389/fmars.2020.00424>
- Paffrath, R., Pahnke, K., Böning, P., Rutgers van der Loeff, M., Valk, O., Gdaniec, S., & Planquette, H. (2021). Seawater-Particle Interactions of Rare Earth Elements and Neodymium Isotopes in the Deep Central Arctic Ocean. *Journal of Geophysical Research: Oceans*, 126(8), e2021JC017423. <https://doi.org/10.1029/2021JC017423>
- Pagano, G., Guida, M., Siciliano, A., Oral, R., Koçbaş, F., Palumbo, A., et al. (2016). Comparative toxicities of selected rare earth elements: Sea urchin embryogenesis and fertilization damage with redox and cytogenetic effects. *Environmental Research*, 147, 453–460. <https://doi.org/10.1016/j.envres.2016.02.031>
- Palmer, M. R. (1985). Rare earth elements in foraminifera tests. *Earth and Planetary Science Letters*, 73(2–4), 285–298. [https://doi.org/10.1016/0012-821X\(85\)90077-9](https://doi.org/10.1016/0012-821X(85)90077-9)
- Palmer, M. R., & Elderfield, H. (1986). Rare earth elements and neodymium isotopes in ferromanganese oxide coatings of Cenozoic foraminifera from the Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 50(3), 409–417. [https://doi.org/10.1016/0016-7037\(86\)90194-8](https://doi.org/10.1016/0016-7037(86)90194-8)
- Pan, F., Xiao, K., Cai, Y., Li, H., Guo, Z., Wang, X., et al. (2023). Integrated effects of bioturbation, warming and sea-level rise on mobility of sulfide and metalloids in sediment porewater of mangrove wetlands. *Water Research*, 233, 119788. <https://doi.org/10.1016/j.watres.2023.119788>
- Pang, X., Li, D., & Peng, A. (2002). Application of rare-earth elements in the agriculture of china and its environmental behavior in soil. *Environmental Science & Pollution Research*, 9(2), 143–148. <https://doi.org/10.1007/BF02987462>
- Paper, M., Koch, M., Jung, P., Lakatos, M., Nilges, T., & Brück, T. B. (2023). Rare earths stick to rare cyanobacteria: Future potential for bioremediation and recovery of rare earth elements. *Frontiers in Bioengineering and Biotechnology*, 11, 1–14. <https://doi.org/10.3389/fbioe.2023.1130939>
- Park, J., Sanford, R. A., & Bethke, C. M. (2006). Geochemical and microbiological zonation of the Middendorf aquifer, South Carolina. *Chemical Geology*, 230(1–2), 88–104. <https://doi.org/10.1016/j.chemgeo.2005.12.001>
- Pathak, P. N., & Choppin, G. R. (2006). Thermodynamic study of metal silicate complexation in perchlorate media. *Radiochimica Acta*, 94(2), 81–86. <https://doi.org/10.1524/ract.2006.94.2.81>
- Pattan, J. N., Pearce, N. J. G., & Mislankar, P. G. (2005). Constraints in using Cerium-anomaly of bulk sediments as an indicator of paleo bottom water redox environment: A case study from the Central Indian Ocean Basin. *Chemical Geology*, 221(3–4), 260–278. <https://doi.org/10.1016/j.chemgeo.2005.06.009>
- Patten, J. T., & Byrne, R. H. (2017). Assessment of Fe(III) and Eu(III) complexation by silicate in aqueous solutions. *Geochimica et Cosmochimica Acta*, 202, 361–373. <https://doi.org/10.1016/j.gca.2016.12.004>
- Patton, G. M., Francois, R., Weis, D., Hathorne, E., Gutjahr, M., Frank, M., & Gordon, K. (2021). An experimental investigation of the acquisition of Nd by authigenic phases of marine sediments. *Geochimica et Cosmochimica Acta*, 301, 1–29. <https://doi.org/10.1016/j.gca.2021.02.010>
- Pavel, C. C., Laca-Arántegui, R., Marmier, A., Schüler, D., Tzimas, E., Buchert, M., et al. (2017). Substitution strategies for reducing the use of rare earths in wind turbines. *Resources Policy*, 52(May), 349–357. <https://doi.org/10.1016/j.resourpol.2017.04.010>
- Pearce, C. R., Jones, M. T., Oelkers, E. H., Pradoux, C., & Jeandel, C. (2013). The effect of particulate dissolution on the neodymium (Nd) isotope and Rare Earth Element (REE) composition of seawater. *Earth and Planetary Science Letters*, 369–370, 138–147. <https://doi.org/10.1016/j.epsl.2013.03.023>
- Pedreira, R. M. A., Pahnke, K., Böning, P., & Hatje, V. (2018). Tracking hospital effluent-derived gadolinium in Atlantic coastal waters off Brazil. *Water Research*, 145, 62–72. <https://doi.org/10.1016/j.watres.2018.08.005>
- Pédrot, M., Dia, A., Davranche, M., & Gruau, G. (2015). Upper soil horizons control the rare earth element patterns in shallow groundwater. *Geoderma*, 239, 84–96. <https://doi.org/10.1016/j.geoderma.2014.09.023>
- Pérez-López, R., Delgado, J., Nieto, J. M., & Márquez-García, B. (2010). Rare earth element geochemistry of sulphide weathering in the São Domingos mine area (Iberian Pyrite Belt): A proxy for fluid-rock interaction and ancient mining pollution. *Chemical Geology*, 276(1), 29–40. <https://doi.org/10.1016/j.chemgeo.2010.05.018>
- Pham, V. Q., Grenier, M., Cravatte, S., Michael, S., Jacquet, S., Belhadj, M., et al. (2019). Dissolved rare earth elements distribution in the Solomon Sea. *Chemical Geology*, 524, 11–36. <https://doi.org/10.1016/j.chemgeo.2019.05.012>
- Pham, V. Q., Jeandel, C., Grenier, M., Cravatte, S., Eldin, G., Belhadj, M., et al. (2022). Neodymium Isotopic Composition and Rare Earth Element Concentration Variations in the Coral and Solomon Seas. *Frontiers in Environmental Chemistry*, 3. <https://doi.org/10.3389/fenvc.2022.803944>



- Picone, N., & den Camp, H. J. O. (2019). Role of rare earth elements in methanol oxidation. *Current Opinion in Chemical Biology*, 49, 39–44. <https://doi.org/10.1016/j.cbpa.2018.09.019>
- Piegras, D. J., & Wasserburg, G. J. (1982). Isotopic composition of neodymium in waters from the Drake Passage. *Science*, 217(4556), 207–217. <https://doi.org/10.1126/science.217.4556.207>
- Piegras, D. J., & Wasserburg, G. J. (1987). Rare earth element transport in the western North Atlantic inferred from Nd isotopic observations. *Geochimica et Cosmochimica Acta*, 51(5), 1257–1271. [https://doi.org/10.1016/0016-7037\(87\)90217-1](https://doi.org/10.1016/0016-7037(87)90217-1)
- Pinto, J., Costa, M., Leite, C., Borges, C., Coppola, F., Henriques, B., et al. (2019). Ecotoxicological effects of lanthanum in *Mytilus galloprovincialis*: Biochemical and histopathological impacts. *Aquatic Toxicology*, 211, 181–192. <https://doi.org/10.1016/j.aquatox.2019.03.017>
- Pinto, J., Henriques, B., Soares, J., Costa, M., Dias, M., Fabre, E., et al. (2020). A green method based on living macroalgae for the removal of rare-earth elements from contaminated waters. *Journal of Environmental Management*, 263, 110376. <https://doi.org/10.1016/j.jenvman.2020.110376>
- Piper, D. Z. (1974). Rare earth elements in the sedimentary cycle: A summary. *Chemical Geology*, 14(4), 285–304. [https://doi.org/10.1016/0009-2541\(74\)90066-7](https://doi.org/10.1016/0009-2541(74)90066-7)
- Pižeta, I., Sander, S. G., Hudson, R. J. M., Omanović, D., Baars, O., Barbeau, K. A., et al. (2015). Interpretation of complexometric titration data: An intercomparison of methods for estimating models of trace metal complexation by natural organic ligands. *Marine Chemistry*, 173, 3–24. <https://doi.org/10.1016/j.marchem.2015.03.006>
- Ponnumani, G., Prakash, R., Srinivasamoorthy, K., & Rajesh Kanna, A. (2022). No title. In V. Senapathi, S. Sekar, P. Viswanathan, & C. Sabarathinam (Eds.), *Groundwater contamination in coastal aquifers: Assessment and management* (pp. 35–54). Elsevier.
- Ponnurangam, A., Bau, M., Brenner, M., & Koschinsky, A. (2016). Mussel shells of *Mytilus edulis* as bioarchives of the distribution of rare earth elements and yttrium in seawater and the potential impact of pH and temperature on their partitioning behavior. *Biogeosciences*, 13(3), 751–760. <https://doi.org/10.5194/bg-13-751-2016>
- Pourmand, A., Dauphas, N., & Ireland, T. J. (2012). A novel extraction chromatography and MC-ICP-MS technique for rapid analysis of REE, Y and Sc: Revising CI-chondrite and Post-Archean Australian Shale (PAAS) abundances. *Chemical Geology*, 291(38–54), 38–54. <https://doi.org/10.1016/j.chemgeo.2011.08.011>
- Pourmand, A., Prospero, J. M., & Sharifi, A. (2014). Geochemical fingerprinting of trans-Atlantic African dust based on radiogenic Sr-Nd-Hf isotopes and rare earth element anomalies. *Geology*, 42(8), 675–678. <https://doi.org/10.1130/G35624.1>
- Pourret, O., Davranche, M., Gruau, G., & Dia, A. (2007). Organic complexation of rare earth elements in natural waters: Evaluating model calculations from ultrafiltration data. *Geochimica et Cosmochimica Acta*, 71(11), 2718–2735. <https://doi.org/10.1016/j.gca.2007.04.001>
- Pourret, O., & Martinez, R. E. (2009). Modeling lanthanide series binding sites on humic acid. *Journal of Colloid and Interface Science*, 330(1), 45–50. <https://doi.org/10.1016/j.jcis.2008.10.048>
- Pourret, O., & Tuduri, J. (2017). Continental shelves as potential resource of rare earth elements. *Scientific Reports*, 7(1), 1–6. <https://doi.org/10.1038/s41598-017-06380-z>
- Prasad, M. B. K., & Ramanathan, A. L. (2008). Distribution of rare earth elements in the Pichavaram mangrove sediments of the southeast coast of India. *Journal of Coastal Research*, 1(24), 126–134. <https://doi.org/10.2112/05-0533.1>
- Prego, R., Caetano, M., Vale, C., & Marmolejo-rodriguez, J. (2009). Rare earth elements in sediments of the Vigo Ria, NW Iberian Peninsula. *Continental Shelf Research*, 29(7), 896–902. <https://doi.org/10.1016/j.csr.2009.01.009>
- Prudêncio, M. I., Valente, T., Marques, R., Sequeira Braga, M. A., & Pamplona, J. (2015). Geochemistry of rare earth elements in a passive treatment system built for acid mine drainage remediation. *Chemosphere*, 138, 691–700. <https://doi.org/10.1016/j.chemosphere.2015.07.064>
- Quadros, A. F., Nordhaus, I., Reuter, H., & Zimmer, M. (2019). Modelling of mangrove annual leaf litterfall with emphasis on the role of vegetation structure. *Estuarine, Coastal and Shelf Science*, 218, 292–299. <https://doi.org/10.1016/j.ecss.2018.12.012>
- Quinn, K. A., Byrne, R. H., & Schijf, J. (2006). Sorption of yttrium and rare earth elements by amorphous ferric hydroxide: Influence of solution complexation with carbonate. *Geochimica et Cosmochimica Acta*, 70(16), 4151–4165. <https://doi.org/10.1016/j.gca.2006.06.014>
- Ragnarsdottir, K. V., Oelkers, E. H., Sherman, D. M., & Collins, C. R. (1998). Aqueous speciation of yttrium at temperatures from 25 to 340°C at P<sub>sat</sub>: An situ EXAFS study. *Chemical Geology*, 151(1–4), 29–39. [https://doi.org/10.1016/S0009-2541\(98\)00068-0](https://doi.org/10.1016/S0009-2541(98)00068-0)
- Ramasamy, D. L., Porada, S., & Sillanpää, M. (2019). Marine algae: A promising resource for the selective recovery of scandium and rare earth elements from aqueous systems. *Chemical Engineering Journal*, 371(April), 759–768. <https://doi.org/10.1016/j.cej.2019.04.106>
- Ramos, S. J., Dinali, G. S., Oliveira, C., Martins, G. C., Moreira, C. G., Siqueira, J. O., & Guilherme, L. R. G. (2016). Rare Earth Elements in the Soil Environment. *Current Pollution Reports*, 2(1), 28–50. <https://doi.org/10.1007/s40726-016-0026-4>
- Raymond, K. N., & Pierre, V. C. (2005). Next generation, high relaxivity gadolinium MRI agents. *Bioconjugate Chemistry*, 16(1), 3–8. <https://doi.org/10.1021/bc049817y>
- Reitz, Z. L., & Medema, M. H. (2022). Genome mining strategies for metallophore discovery. *Current Opinion in Biotechnology*, 77(liv), 102757. <https://doi.org/10.1016/j.copbio.2022.102757>
- Rempfer, J., Stocker, T. F., Joos, F., Dutay, J., & Siddall, M. (2011). Modelling Nd-isotopes with a coarse resolution ocean circulation model: Sensitivities to model parameters and source/sink distributions. *Geochimica et Cosmochimica Acta*, 75(20), 5927–5950. <https://doi.org/10.1016/j.gca.2011.07.044>
- Rétif, J., Zalouk-Vergnoux, A., Briant, N., & Poirier, L. (2023). From geochemistry to ecotoxicology of rare earth elements in aquatic environments: Diversity and uses of normalization reference materials and anomaly calculation methods. *Science of the Total Environment*, 856, 158890. <https://doi.org/10.1016/j.scitotenv.2022.158890>
- Reynard, B., Lécuyer, C., & Grandjean, P. (1999). Crystal-chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. *Chemical Geology*, 155(3–4), 233–241. [https://doi.org/10.1016/S0009-2541\(98\)00169-7](https://doi.org/10.1016/S0009-2541(98)00169-7)
- Rickli, J., Gutjahr, M., Vance, D., Fischer-Gödde, M., Hillenbrand, C. D., & Kuhn, G. (2014). Neodymium and hafnium boundary contributions to seawater along the West Antarctic continental margin. *Earth and Planetary Science Letters*, 394, 99–110. <https://doi.org/10.1016/j.epsl.2014.03.008>
- Riglet-Martial, C., Vitorge, P., & Calmon, V. (1998). Electrochemical characterisation of the Ce(IV) limiting carbonate complex. *Radiochimica Acta*, 82(special-issue.69), 69–76. <https://doi.org/10.1524/ract.1998.82>
- Robinson, S., Ivanovic, R., van de Flierdt, T., Blanchet, C. L., Tachikawa, K., Martin, E. E., et al. (2021). Global continental and marine detrital εNd: An updated compilation for use in understanding marine Nd cycling. *Chemical Geology*, 567, 120119. <https://doi.org/10.1016/j.chemgeo.2021.120119>
- Rocha, C. (1998). Rhythmic ammonium regeneration and flushing in intertidal sediments of the Sado estuary. *Limnology & Oceanography*, 43(5), 823–831. <https://doi.org/10.4319/lo.1998.43.5.0823>
- Rogowska, J., Olkowska, E., Ratajczyk, W., & Wolska, L. (2018). Gadolinium as a New Emerging Contaminant of Aquatic Environments. *Environmental Toxicology and Chemistry*, 37(6), 1523–1534. <https://doi.org/10.1002/etc.4116>

- Romero, F. M., Prol-Ledesma, R. M., Canet, C., Alvares, L. N., & Pérez-Vázquez, R. (2010). Acid drainage at the inactive Santa Lucia mine, western Cuba: Natural attenuation of arsenic, barium and lead, and geochemical behavior of rare earth elements. *Applied Geochemistry*, 25(5), 716–727. <https://doi.org/10.1016/j.apgeochem.2010.02.004>
- Rönnback, P., Åström, M., & Gustafsson, J. P. (2008). Comparison of the behaviour of rare earth elements in surface waters, overburden groundwaters and bedrock groundwaters in two granitoidic settings, Eastern Sweden. *Applied Geochemistry*, 23(7), 1862–1880. <https://doi.org/10.1016/j.apgeochem.2008.02.008>
- Rousseau, T., Sonke, J., Chmieleff, J., Van Beek, P., Souhaut, M., Boaventura, G., et al. (2015). Rapid neodymium release to marine waters from lithogenic sediments in the Amazon estuary. *Nature Communications*, 6(May), 7592. <https://doi.org/10.1038/ncomms8592>
- Roy, M., Martin, J. B., Cable, J. E., & Smith, C. G. (2013). Variations of iron flux and organic carbon remineralization in a subterranean estuary caused by inter-annual variations in recharge. *Geochimica et Cosmochimica Acta*, 103, 301–315. <https://doi.org/10.1016/j.gca.2012.10.055>
- Roy, M., Martin, J. B., Cherrier, J., Cable, J. E., & Smith, C. G. (2010). Influence of sea level rise on iron diagenesis in an east Florida subterranean estuary. *Geochimica et Cosmochimica Acta*, 74(19), 5560–5573. <https://doi.org/10.1016/j.gca.2010.07.007>
- Roy, M., Martin, J. B., Smith, C. G., & Cable, J. E. (2011). Reactive-transport modeling of iron diagenesis and associated organic carbon remineralization in a Florida (USA) subterranean estuary. *Earth and Planetary Science Letters*, 304(1–2), 191–201. <https://doi.org/10.1016/j.epsl.2011.02.002>
- Rudnick, R., & Gao, S. (2003). 3.1 Composition of the Continental Crust. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on geochemistry* (First Edition, Vol. 3: The Cru, pp. 1–64). : Elsevier-Pergamon. <https://doi.org/10.1016/B0-08-043751-6/03016-4>
- Rue, G., & McKnight, D. (2021). Enhanced rare earth element mobilization in a mountain watershed of the Colorado Mineral Belt with concomitant detection in aquatic biota: Increasing climate change-driven degradation to water quality. *Environmental Science and Technology*, 55(21), 14378–14388. <https://doi.org/10.1021/acs.est.1c02958>
- Santos, A. C. S. S., Souza, L. A., Araujo, T. G., de Rezende, C. E., & Hatje, V. (2023). Fate and trophic transfer of rare earth elements in a tropical estuarine food web. *Environmental Science and Technology*, 57(6), 2404–2414. <https://doi.org/10.1021/acs.est.2c07726>
- Santos-Echeandía, J., Vale, C., Caetano, M., Pereira, P., & Prego, R. (2010). Effect of tidal flooding on metal distribution in pore waters of marsh sediments and its transport to water column (Tagus estuary, Portugal). *Marine Environmental Research*, 70(5), 358–367. <https://doi.org/10.1016/j.marenvres.2010.07.003>
- Sappal, S. M., Ramanathan, A., Ranjan, R. K., Singh, G., & Kumar, A. (2014). Rare Earth Elements As Biogeochemical Indicators In Mangrove Ecosystems (Pichavaram, Tamilnadu, India). *Journal of Sedimentary Research*, 84(9), 781–791. <https://doi.org/10.2110/jsr.2014.63>
- Schaller, J. (2014). Bioturbation/bioirrigation by Chironomus plumosus as main factor controlling elemental remobilization from aquatic sediments? *Chemosphere*, 107, 336–343. <https://doi.org/10.1016/j.chemosphere.2013.12.086>
- Schau, M., & Henderson, J. B. (1983). Archean chemical weathering at three localities on the Canadian shield. *Precambrian Research*, 20(C), 189–224. [https://doi.org/10.1016/S0166-2635\(08\)70243-3](https://doi.org/10.1016/S0166-2635(08)70243-3)
- Schijf, J., & Byrne, R. H. (2001). Stability constants for mono- and dioxalato-complexes of Y and the REE, potentially important species in groundwaters and surface freshwaters. *Geochimica et Cosmochimica Acta*, 65(7), 1037–1046. [https://doi.org/10.1016/S0016-7037\(00\)00591-3](https://doi.org/10.1016/S0016-7037(00)00591-3)
- Schijf, J., & Byrne, R. H. (2004). Determination of SO<sub>4</sub>B1 for yttrium and the rare earth elements at I = 0.66 m and t = 25°C—Implications for YREE solution speciation in sulfate-rich waters. *Geochimica et Cosmochimica Acta*, 68(13), 2825–2837. <https://doi.org/10.1016/j.gca.2003.12.003>
- Schijf, J., & Byrne, R. H. (2008). Comment on “An experimental study of the solubility and speciation of neodymium (III) fluoride in F-bearing aqueous solutions” by A.A. Migdisov and A.E. Williams-Jones. *Geochimica et Cosmochimica Acta*, 72(22), 5574–5577. <https://doi.org/10.1016/j.gca.2008.06.032>
- Schijf, J., & Byrne, R. H. (2021). Speciation of yttrium and the rare earth elements in seawater: Review of a 20-year analytical journey. *Chemical Geology*, 585, 120479. <https://doi.org/10.1016/j.chemgeo.2021.120479>
- Schijf, J., Christenson, E. A., & Byrne, R. H. (2015). YREE scavenging in seawater: A new look at an old model. *Marine Chemistry*, 177, 460–471. <https://doi.org/10.1016/j.marchem.2015.06.010>
- Schijf, J., de Baar, H. J. W., & Millero, F. J. (1994). Kinetics of Ce and Nd scavenging in Black Sea waters. *Marine Chemistry*, 46(4), 345–359. [https://doi.org/10.1016/0304-4203\(94\)90031-0](https://doi.org/10.1016/0304-4203(94)90031-0)
- Schijf, J., de Baar, H. J. W., & Millero, F. J. (1995). Vertical distributions and speciation of dissolved rare earth elements in the anoxic brines of Bannock Basin, eastern Mediterranean Sea. *Geochimica et Cosmochimica Acta*, 59(16), 3285–3299. [https://doi.org/10.1016/0016-7037\(95\)00219-P](https://doi.org/10.1016/0016-7037(95)00219-P)
- Schijf, J., & Marshall, K. S. (2011). YREE sorption on hydrous ferric oxide in 0.5M NaCl solutions: A model extension. *Marine Chemistry*, 123(1–4), 32–43. <https://doi.org/10.1016/j.marchem.2010.09.003>
- Schijf, J., & Zoll, A. M. (2011). When dissolved is not truly dissolved—The importance of colloids in studies of metal sorption on organic matter. *Journal of Colloid and Interface Science*, 361(1), 137–147. <https://doi.org/10.1016/j.jcis.2011.05.029>
- Schmidt, K., Bau, M., Merschel, G., & Tepe, N. (2019). Anthropogenic gadolinium in tap water and in tap water-based beverages from fast-food franchises in six major cities in Germany. *Science of the Total Environment*, 687, 1401–1408. <https://doi.org/10.1016/j.scitotenv.2019.07.075>
- Schüler, D., Buchert, M., Liu, R., Dittrich, S., & Merz, C. (2011). Study on rare earths and their recycling. *Öko-Institut eV Darmstadt*, 49, 30–40.
- Seto, M., & Akagi, T. (2008). Chemical conditions for the appearance of a negative Ce anomaly in stream waters and groundwaters. *Geochemical Journal*, 42(4), 371–380. <https://doi.org/10.2343/geochemj.42.371>
- Sharifi, R., Moore, F., & Keshavarzi, B. (2013). Geochemical behavior and speciation modeling of rare earth elements in acid drainages at Sarcheshmeh porphyry copper deposit, Kerman Province, Iran. *Chemie der Erde*, 73(4), 509–517. <https://doi.org/10.1016/j.chemer.2013.03.001>
- Shaw, H. F., & Wasserburg, G. J. (1985). Sm-Nd in marine carbonates and phosphates: Implications for Nd isotopes in seawater and crustal ages. *Geochimica et Cosmochimica Acta*, 49(2), 503–518. [https://doi.org/10.1016/0016-7037\(85\)90042-0](https://doi.org/10.1016/0016-7037(85)90042-0)
- Shields, G., & Stille, P. (2001). Diagenetic constraints on the use of cerium anomalies as palaeoseawater redox proxies: An isotopic and REE study of Cambrian phosphorites. *Chemical Geology*, 175(1–2), 29–48. [https://doi.org/10.1016/S0009-2541\(00\)00362-4](https://doi.org/10.1016/S0009-2541(00)00362-4)
- Shiller, A. M., Chan, E., Joung, D., Redmond, M., & Kessler, J. (2017). Light rare earth element depletion during Deepwater Horizon blowout methanotrophy. *Scientific Reports*, 7, 1–9. <https://doi.org/10.1038/s41598-017-11060-z>
- Sholkovitz, E. R. (1978). The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. *Earth and Planetary Science Letters*, 41(1), 77–86. [https://doi.org/10.1016/0012-821X\(78\)90043-2](https://doi.org/10.1016/0012-821X(78)90043-2)
- Sholkovitz, E. R. (1992). Chemical evolution of rare earth elements: Fractionation between colloidal and solution phases of filtered river water. *Earth and Planetary Science Letters*, 114(1), 77–84. [https://doi.org/10.1016/0012-821X\(92\)90152-L](https://doi.org/10.1016/0012-821X(92)90152-L)
- Sholkovitz, E. R. (1993). The geochemistry of rare earth elements in the Amazon River estuary. *Geochimica et Cosmochimica Acta*, 57(10), 2181–2190. [https://doi.org/10.1016/0016-7037\(93\)90559-F](https://doi.org/10.1016/0016-7037(93)90559-F)

- Sholkovitz, E. R. (1995). The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquatic Geochemistry*, 1(1), 1–34. <https://doi.org/10.1007/BF01025229>
- Sholkovitz, E. R., Boyle, E. A., & Price, N. B. (1978). The removal of dissolved humic acids and iron during estuarine mixing. *Earth and Planetary Science Letters*, 40(1), 130–136. [https://doi.org/10.1016/0012-821X\(78\)90082-1](https://doi.org/10.1016/0012-821X(78)90082-1)
- Sholkovitz, E. R., Landing, W. M., & Lewis, B. L. (1994). Ocean particle chemistry: The fractionation of rare earth elements between suspended particles and seawater. *Geochimica et Cosmochimica Acta*, 58(6), 1567–1579. [https://doi.org/10.1016/0016-7037\(94\)90559-2](https://doi.org/10.1016/0016-7037(94)90559-2)
- Sholkovitz, E. R., Piegras, D. J., & Jacobsen, S. B. (1989). The pore water chemistry of rare earth elements in Buzzard Bay sediments. *Geochimica et Cosmochimica Acta*, 53(11), 2847–2856. [https://doi.org/10.1016/0016-7037\(89\)90162-2](https://doi.org/10.1016/0016-7037(89)90162-2)
- Sholkovitz, E. R., Shaw, T. J., & Schneider, D. L. (1992). The geochemistry of rare earth elements in the seasonally anoxic water column and porewaters of Chesapeake Bay. *Geochimica et Cosmochimica Acta*, 56(9), 3389–3402. [https://doi.org/10.1016/0016-7037\(92\)90386-W](https://doi.org/10.1016/0016-7037(92)90386-W)
- Sholkovitz, E. R., & Szymczak, R. (2000). The estuarine chemistry of rare earth elements: Comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. *Earth and Planetary Science Letters*, 179(2), 299–309. [https://doi.org/10.1016/S0012-821X\(00\)00112-6](https://doi.org/10.1016/S0012-821X(00)00112-6)
- Siddall, M., Khatiwala, S., van de Flierdt, T., Jones, K., Goldstein, S. L., Hemming, S., & Anderson, R. F. (2008). Towards explaining the Nd paradox using reversible scavenging in an ocean general circulation model. *Earth and Planetary Science Letters*, 274(3–4), 448–461. <https://doi.org/10.1016/j.epsl.2008.07.044>
- Silva, F. B. V., Nascimento, C. W. A., Alvarez, A. M., & Araújo, P. R. M. (2019). Inputs of rare earth elements in Brazilian agricultural soils via P-containing fertilizers and soil correctives. *Journal of Environmental Management*, 232, 90–96. <https://doi.org/10.1016/j.jenvman.2018.11.031>
- Silva, R., & Nitsche, H. (1995). Actinide Environmental Chemistry. *Radiochimica Acta*, 70–77(Supplement), 377–396. <https://doi.org/10.1524/ract.1995.7071.special-issue.377>
- Silva-Filho, E. V., Sanders, C. J., Bernat, M., Figueiredo, A. M. G., Sella, S. M., & Wasserman, J. (2011). Origin of rare earth element anomalies in mangrove sediments, Sepetiba Bay, SE Brazil: Used as geochemical tracers of sediment sources. *Environmental Earth Sciences*, 64(5), 1257–1267. <https://doi.org/10.1007/s12665-011-0942-y>
- Simon, N. S. (1989). Nitrogen cycling between sediment and the shallow-water column in the transition zone of the Potomac River and Estuary. II. The role of wind-driven resuspension and adsorbed ammonium. *Estuarine, Coastal and Shelf Science*, 28(5), 531–547. [https://doi.org/10.1016/0272-7714\(89\)90028-0](https://doi.org/10.1016/0272-7714(89)90028-0)
- Singh, S. P., Singh, S. K., Goswami, V., Bhushan, R., & Rai, V. K. (2012). Spatial distribution of dissolved neodymium and εNd in the Bay of Bengal: Role of particulate matter and mixing of water masses. *Geochimica et Cosmochimica Acta*, 94, 38–56. <https://doi.org/10.1016/j.gca.2012.07.017>
- Skinner, L. C., Sadekov, A., Brandon, M., Greaves, M., Plancherel, Y., de la Fuente, M., et al. (2019). Rare Earth Elements in early-diagenetic foraminifer ‘coatings’: Pore-water controls and potential palaeoceanographic applications. *Geochimica et Cosmochimica Acta*, 245, 118–132. <https://doi.org/10.1016/j.gca.2018.10.027>
- Smedley, P. L. (1991). The geochemistry of rare earth elements in groundwater from the Carnmenellis area, southwest England. *Geochimica et Cosmochimica Acta*, 55(10), 2767–2779. [https://doi.org/10.1016/0016-7037\(91\)90443-9](https://doi.org/10.1016/0016-7037(91)90443-9)
- Smirnova, E. V., Mysovskaya, I. N., Lozhkin, V. I., Sandimirova, G. P., Pakhomova, N. N., & Smagunova, A. A. (2006). Spectral interferences from polyatomic barium ions in inductively coupled plasma mass spectrometry. *Journal of Applied Spectroscopy*, 73(6), 911–917. <https://doi.org/10.1007/s10812-006-0175-0>
- Soli, A. L., & Byrne, R. H. (2017). Europium silicate complexation at 25°C and 0.7 molar ionic strength. *Marine Chemistry*, 195, 138–142. <https://doi.org/10.1016/j.marchem.2017.02.006>
- Sousa, T. A., Venancio, I. M., Marques, E. D., Figueiredo, T. S., Nascimento, R. A., Smoak, J. M., et al. (2022). REE anomalies changes in bottom sediments applied in the western equatorial Atlantic since the last interglacial. *Frontiers in Marine Science*, 9, 1–14. <https://doi.org/10.3389/fmars.2022.846976>
- Souza, L. A., Pedreira, R. M. A., Miró, M., & Hatje, V. (2021). Evidence of high bioaccessibility of gadolinium-contrast agents in natural waters after human oral uptake. *Science of the Total Environment*, 793, 148506. <https://doi.org/10.1016/j.scitotenv.2021.148506>
- Soyol-Erdene, T. O., Valente, T., Grande, J. A., & de la Torre, M. L. (2018). Mineralogical controls on mobility of rare earth elements in acid mine drainage environments. *Chemosphere*, 205, 317–327. <https://doi.org/10.1016/j.chemosphere.2018.04.095>
- Squadrone, S., Brizio, P., Battuello, M., Nurra, N., Sartor, R. M., Benedetto, A., et al. (2017). A first report of rare earth elements in northwestern Mediterranean seaweeds. *Marine Pollution Bulletin*, 122(1–2), 236–242. <https://doi.org/10.1016/j.marpolbul.2017.06.048>
- Squadrone, S., Brizio, P., Stella, C., Mantia, M., Favaro, L., Biancani, B., et al. (2020). Differential bioaccumulation of trace elements and rare earth elements in the muscle, kidneys, and liver of the invasive Indo-Pacific Lionfish (Pterois spp.) from Cuba. *Biological Trace Element Research*, 196(1), 262–271. <https://doi.org/10.1007/s12011-019-01918-w>
- Squadrone, S., Nurra, N., Battuello, M., Mussat Sartor, R., Stella, C., Brizio, P., et al. (2018). Trace elements, rare earth elements and inorganic arsenic in seaweeds from Giglio Island (Thyrrhenian Sea) after the Costa Concordia shipwreck and removal. *Marine Pollution Bulletin*, 133, 88–95. <https://doi.org/10.1016/j.marpolbul.2018.05.028>
- Stanley, J., & Byrne, R. (1990). The influence of solution chemistry on REE uptake by *Ulva Lactuca* L. in seawater. *Geochimica et Cosmochimica Acta*, 54(6), 1587–1595. [https://doi.org/10.1016/0016-7037\(90\)90393-Y](https://doi.org/10.1016/0016-7037(90)90393-Y)
- Stetzenbach, K. J., Amano, M., Kreamer, D. K., & Hodge, V. F. (1994). Testing the limits of ICP-MS determination of trace elements in ground water at the parts-per-trillion level. *Ground Water*, 32(6), 976–985. <https://doi.org/10.1111/j.1745-6584.1994.tb00937.x>
- Stetzenbach, K. J., Hodge, V. F., Guo, C., Farnham, I. M., & Johannesson, K. H. (2001). Geochemical and statistical evidence of deep carbonate groundwater within overlying volcanic rock aquifers/aquifers of southern Nevada, USA. *Journal of Hydrology*, 243(3–4), 254–271. [https://doi.org/10.1016/S0022-1694\(00\)00418-2](https://doi.org/10.1016/S0022-1694(00)00418-2)
- Stichel, T., Hartman, A. E., Duggan, B., Goldstein, S. L., Scher, H., & Pahnke, K. (2015). Separating biogeochemical cycling of neodymium from water mass mixing in the Eastern North Atlantic. *Earth and Planetary Science Letters*, 412, 245–260. <https://doi.org/10.1016/j.epsl.2014.12.008>
- Stichel, T., Pahnke, K., Duggan, B., Goldstein, S. L., Hartman, A. E., Paffrath, R., & Scher, H. D. (2018). TAG plume: Revisiting the hydrothermal neodymium contribution to seawater. *Frontiers in Marine Science*, 5, 96. <https://doi.org/10.3389/fmars.2018.00096>
- Stolpe, B., Guo, L., & Shiller, A. M. (2013). Binding and transport of rare earth elements by organic and iron-rich nanocolloids in alaskan rivers, as revealed by field-flow fractionation and ICP-MS. *Geochimica et Cosmochimica Acta*, 106, 446–462. <https://doi.org/10.1016/j.gca.2012.12.033>
- Sundby, B., Vale, C., Caetano, M., & Luther III, G. W. (2003). Redox Chemistry in the Root Zone of a Salt Marsh Sediment in the Tagus Estuary, Portugal. *Aquatic Geochemistry*, 9(3), 257–271. <https://doi.org/10.1023/B:AQUA.0000022957.42522.9a>
- Sutorius, M., Mori, C., Greskowiak, J., Boettcher, L., Bunse, C., Dittmar, T., et al. (2022). Rare earth element behaviour in seawater under the influence of organic matter cycling during a phytoplankton spring bloom – A mesocosm study. *Frontiers in Marine Science*, 9, 1–20. <https://doi.org/10.3389/fmars.2022.895723>

- Sverjensky, D. A. (1984). Europium redox equilibria in aqueous solution. *Earth and Planetary Science Letters*, 67(1), 70–78. [https://doi.org/10.1016/0012-821X\(84\)90039-6](https://doi.org/10.1016/0012-821X(84)90039-6)
- Tachikawa, K., Arsouze, T., Bayon, G., Bory, A., Colin, C., Dutay, J. C., et al. (2017). The large-scale evolution of neodymium isotopic composition in the global modern and Holocene ocean revealed from seawater and archive data. *Chemical Geology*, 457, 131–148. <https://doi.org/10.1016/j.chemgeo.2017.03.018>
- Tachikawa, K., Athias, V., & Jeandel, C. (2003). Neodymium budget in the modern ocean and paleo-oceanographic implications. *Journal of Geophysical Research*, 108(C8), 3254. <https://doi.org/10.1029/1999JC000285>
- Tachikawa, K., Jeandel, C., & Roy-Barman, M. (1999). A new approach to the Nd residence time in the ocean: The role of atmospheric inputs. *Earth and Planetary Science Letters*, 170(4), 433–446. [https://doi.org/10.1016/S0012-821X\(99\)00127-2](https://doi.org/10.1016/S0012-821X(99)00127-2)
- Tachikawa, K., Jeandel, C., Vangriesheim, A., & Dupré, B. (1999). Distribution of rare earth elements and neodymium isotopes in suspended particles of the tropical Atlantic Ocean (EUMELI site). *Deep-Sea Research Part I Oceanographic Research Papers*, 46(5), 733–755. [https://doi.org/10.1016/S0967-0637\(98\)00089-2](https://doi.org/10.1016/S0967-0637(98)00089-2)
- Tachikawa, K., Toyofuku, T., Basile-Doelsch, I., & Delhaye, T. (2013). Microscale neodymium distribution in sedimentary planktonic foraminiferal tests and associated mineral phases. *Geochimica et Cosmochimica Acta*, 100, 11–23. <https://doi.org/10.1016/j.gca.2012.10.010>
- Taillefert, M., Neuhuber, S., & Bristow, G. (2007). The effect of tidal forcing on biogeochemical processes in intertidal salt marsh sediments. *Geochemical Transactions*, 8, 1–15. <https://doi.org/10.1186/1467-4866-8-6>
- Takahashi, Y., Châtellier, X., Hattori, K. H., Kato, K., & Fortin, D. (2005). Adsorption of rare earth elements onto bacterial cell walls and its implication for REE sorption onto natural microbial mats. *Chemical Geology*, 219(1–4), 53–67. <https://doi.org/10.1016/j.chemgeo.2005.02.009>
- Takahashi, Y., Hayasaka, Y., Morita, K., Kashiwabara, T., Nakada, R., Marcus, M. A., et al. (2015). Transfer of rare earth elements (REE) from manganese oxides to phosphates during early diagenesis in pelagic sediments inferred from REE patterns, X-ray absorption spectroscopy, and chemical leaching method. *Geochemical Journal*, 49(6), 653–674. <https://doi.org/10.2343/geochemj.2.0393>
- Takahashi, Y., Manceau, A., Geoffroy, N., Marcus, M. A., & Usui, A. (2007). Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides. *Geochimica et Cosmochimica Acta*, 71(4), 984–1008. <https://doi.org/10.1016/j.gca.2006.11.016>
- Takahashi, Y., Sakami, H., & Nomura, M. (2002). Determination of the oxidation state of cerium in rocks by Ce LIII-edge X-ray absorption near-edge structure spectroscopy. *Analytica Chimica Acta*, 468(2), 345–354. [https://doi.org/10.1016/S0003-2670\(02\)00709-2](https://doi.org/10.1016/S0003-2670(02)00709-2)
- Takahashi, Y., Shimizu, H., Usui, A., Kagi, H., & Nomura, M. (2000). Direct observation of tetravalent cerium in ferromanganese nodules and crusts by X-ray-absorption near-edge structure (XANES). *Geochimica et Cosmochimica Acta*, 64(17), 2929–2935. [https://doi.org/10.1016/S0016-7037\(00\)00403-8](https://doi.org/10.1016/S0016-7037(00)00403-8)
- Takahashi, Y., Yoshida, H., Sato, N., Hama, K., Yusa, Y., & Shimizu, H. (2002). W- and M-type tetrad effects in REE patterns for water-rock systems in the Tono uranium deposit, central Japan. *Chemical Geology*, 184(3–4), 311–335. [https://doi.org/10.1016/S0009-2541\(01\)00388-6](https://doi.org/10.1016/S0009-2541(01)00388-6)
- Takaya, Y., Yasukawa, K., Kawasaki, T., FujiTakaya, Y., Yasukawa, K., Kawasaki, T., et al. (2018). The tremendous potential of deep-sea mud as a source of rare-earth elements. *Scientific Reports*, 8(1), 5763. <https://doi.org/10.1038/s41598-018-23948-5>
- Tan, Q., Li, J., & Zeng, X. (2015). Rare Earth Elements Recovery from Waste Fluorescent Lamps: A Review. *Critical Reviews in Environmental Science and Technology*, 45(7), 749–776. <https://doi.org/10.1080/10643389.2014.900240>
- Tanaka, K., Tani, Y., Takahashi, Y., Tanimizu, M., Suzuki, Y., Kozai, N., & Ohnuki, T. (2010). A specific Ce oxidation process during sorption of rare earth elements on biogenic Mn oxide produced by *Acremonium* sp. strain KR21-2. *Geochimica et Cosmochimica Acta*, 74(19), 5463–5477. <https://doi.org/10.1016/j.gca.2010.07.010>
- Tang, J., & Johannesson, K. H. (2003). Speciation of rare earth elements in natural terrestrial waters: Assessing the role of dissolved organic matter from the modeling approach. *Geochimica et Cosmochimica Acta*, 67(13), 2321–2339. [https://doi.org/10.1016/S0016-7037\(02\)01413-8](https://doi.org/10.1016/S0016-7037(02)01413-8)
- Tang, J., & Johannesson, K. H. (2005). Adsorption of rare earth elements onto Carrizo sand: Experimental investigations and modeling with surface complexation. *Geochimica et Cosmochimica Acta*, 69(22), 5247–5261. <https://doi.org/10.1016/j.gca.2005.06.021>
- Tang, J., & Johannesson, K. H. (2006). Controls on the geochemistry of rare earth elements along a groundwater flow path in the Carrizo Sand aquifer, Texas, USA. *Chemical Geology*, 225(1–2), 156–171. <https://doi.org/10.1016/j.chemgeo.2005.09.007>
- Tang, J., & Johannesson, K. H. (2010). Ligand extraction of rare earth elements from aquifer sediments: Implications for rare earth element complexation with organic matter in natural waters. *Geochimica et Cosmochimica Acta*, 74(23), 6690–6705. <https://doi.org/10.1016/j.gca.2010.08.028>
- Tao, Z., Wang, X., Guo, Z., & Chu, T. (2004). Is there a tetrad effect in the adsorption of lanthanides (III) at solid-water interfaces? *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 251(1–3), 19–25. <https://doi.org/10.1016/j.colsurfa.2004.08.078>
- Tariq, H., Sharma, A., Sarkar, S., Ojha, L., Pal, R. P., & Mani, V. (2020). Perspectives for rare earth elements as feed additive in livestock - A review. *Asian-Australasian Journal of Animal Sciences*, 33(3), 373–381. <https://doi.org/10.5713/ajas.19.0242>
- Taunton, A. E., Welch, S. A., & Banfield, J. F. (2000). Geomicrobiological controls on light rare earth element, Y and Ba distributions during granite weathering and soil formation. *Journal of Alloys and Compounds*, 303–304, 30–36. [https://doi.org/10.1016/S0925-8388\(00\)00597-1](https://doi.org/10.1016/S0925-8388(00)00597-1)
- Taylor, S. R., & McLennan, S. M. (1985). The continental crust: Its composition and evolution.
- Taylor, S. R., & McLennan, S. M. (2002). Chemical composition and element distribution in the Earth's crust. In *Encyclopedia of physical science and technology* (3rd ed., pp. 697–719). Academic Press. <https://doi.org/10.1016/b0-12-227410-5/00097-1>
- Telgmann, L., Sperling, M., & Karst, U. (2013). Determination of gadolinium-based MRI contrast agents in biological and environmental samples: A review. *Analytica Chimica Acta*, 764, 1–16. <https://doi.org/10.1016/j.aca.2012.12.007>
- Tepe, N., Romero, M., & Bau, M. (2014). High-technology metals as emerging contaminants: Strong increase of anthropogenic gadolinium levels in tap water of Berlin, Germany, from 2009 to 2012. *Applied Geochemistry*, 45, 191–197. <https://doi.org/10.1016/j.apgeochem.2014.04.006>
- Thakur, P., Singh, D. K., & Choppin, G. R. (2007). Polymerization study of o-Si(OH)<sub>4</sub> and complexation with Am(III), Eu(III) and Cm(III). *Inorganica Chimica Acta*, 360(12), 3705–3711. <https://doi.org/10.1016/j.ica.2007.04.051>
- Thomas, P. J., Carpenter, D., Boutin, C., & Allison, J. E. (2014). Rare earth elements (REEs): Effects on germination and growth of selected crop and native plant species. *Chemosphere*, 96, 57–66. <https://doi.org/10.1016/j.chemosphere.2013.07.020>
- Till, C. P., Shelley, R. U., Landing, W. M., & Bruland, K. W. (2017). Dissolved scandium, yttrium, and lanthanum in the surface waters of the North Atlantic: Potential use as an indicator of scavenging intensity. *Journal of Geophysical Research: Oceans*, 122(8), 6684–6697. <https://doi.org/10.1002/2017JC012696>
- Tommasi, F., Thomas, P. J., Lyons, D. M., Pagano, G., Oral, R., Siciliano, A., et al. (2023). Evaluation of Rare Earth Element-Associated Hormetic Effects in Candidate Fertilizers and Livestock Feed Additives. *Biological Trace Element Research*, 201(5), 2573–2581. <https://doi.org/10.1007/s12011-022-03331-2>

- Tommasi, F., Thomas, P. J., Pagano, G., Perono, G. A., Oral, R., Lyons, D. M., et al. (2021). Review of Rare Earth Elements as Fertilizers and Feed Additives: A Knowledge Gap Analysis. *Archives of Environmental Contamination and Toxicology*, 81(4), 531–540. <https://doi.org/10.1007/s00244-020-00773-4>
- Tostevin, R., Shields, G. A., Tarbuck, G. M., He, T., Clarkson, M. O., & Wood, R. A. (2016). Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine settings. *Chemical Geology*, 438, 146–162. <https://doi.org/10.1016/j.chemgeo.2016.06.027>
- Toyoda, K., & Tokonami, M. (1990). Diffusion of rare-earth elements in fish teeth from deep-sea sediments. *Nature*, 345(6276), 607–609. <https://doi.org/10.1038/345607a0>
- Tsuruta, T. (2006). Selective accumulation of light or heavy rare earth elements using gram-positive bacteria. *Colloids and Surfaces B: Biointerfaces*, 52(2), 117–122. <https://doi.org/10.1016/j.colsurfb.2006.04.014>
- Turner, D. R., Whitfield, M., & Dickson, A. G. (1981). The equilibrium speciation of dissolved components in freshwater and sea water at 25°C and 1 atm pressure. *Geochimica et Cosmochimica Acta*, 45(6), 855–881. [https://doi.org/10.1016/0016-7037\(81\)90115-0](https://doi.org/10.1016/0016-7037(81)90115-0)
- Turra, C. (2018). Sustainability of rare earth elements chain: From production to food—a review. *International Journal of Environmental Health Research*, 28(1), 23–42. <https://doi.org/10.1080/09603123.2017.1415307>
- Turra, C., Fernandes, E. A. D. N., & Bacchi, M. A. (2011). Evaluation on rare earth elements of Brazilian agricultural supplies. *Journal of Environmental Chemistry and Ecotoxicology*, 3(4), 86–92.
- Tweed, S. O., Weaver, T. R., Cartwright, I., & Schaefer, B. (2006). Behavior of rare earth elements in groundwater during flow and mixing in fractured rock aquifers: An example from the Dandenong Ranges, southeast Australia. *Chemical Geology*, 234(3–4), 291–307. <https://doi.org/10.1016/j.chemgeo.2006.05.006>
- Tyler, G. (2004). Rare earth elements in soil and plant systems - A review. *Plant and Soil*, 267(1–2), 191–206. <https://doi.org/10.1007/s11104-005-4888-2>
- Vale, C., & Sundby, B. (1998). The interactions between living organisms and metals in intertidal and subtidal sediments. In *Metal metabolism in aquatic environments* (pp. 19–29). Springer US. [https://doi.org/10.1007/978-1-4757-2761-6\\_2](https://doi.org/10.1007/978-1-4757-2761-6_2)
- van de Fliert, T., Franck, M., Lee, D., Halliday, A., Reynolds, B., & Hein, J. (2004). New constraints on the sources and behavior of neodymium and hafnium in seawater from Pacific Ocean ferromanganese crusts. *Geochimica et Cosmochimica Acta*, 68(19), 3827–3843. <https://doi.org/10.1016/j.gca.2004.03.009>
- van de Fliert, T., Griffiths, A. M., Lamblet, M., Little, S. H., Stichel, T., & Wilson, D. J. (2016). Neodymium in the oceans: A global database, a regional comparison and implications for palaeoceanographic research. *Philosophical Transactions of the Royal Society A: Mathematical, Physical & Engineering Sciences*, 374(2081), 20150293. <https://doi.org/10.1098/rsta.2015.0293>
- Volokh, A. A., Gorbunov, A. V., Gundorina, S. F., Revich, B. A., Frontasyeva, M. V., & Chen, S. P. (1990). Phosphorus fertilizer production as a source of rare-earth elements pollution of the environment. *Science of the Total Environment*, 95(C), 141–148. [https://doi.org/10.1016/0048-9697\(90\)90059-4](https://doi.org/10.1016/0048-9697(90)90059-4)
- von Blanckenburg, F. (1999). Tracing Past Ocean Circulation? *Science*, 286(5446), 1862–1863. <https://doi.org/10.1126/science.286.5446.1862>
- Voutsinos, M., Banfield, J. F., & McClelland, H. O. (2023). Extensive and diverse lanthanide-dependent metabolism in the ocean. <https://doi.org/10.1101/2023.07.25.550467>
- Voutsinos, M. Y., West-Roberts, J. A., Sachdeva, R., Moreau, J. W., & Banfield, J. F. (2022). Do lanthanide-dependent microbial metabolisms drive the release of REEs from weathered granites? *bioRxiv*, 2022–2103. <https://doi.org/10.1101/2022.03.08.483559>
- Vraspir, J. M., & Butler, A. (2009). Chemistry of marine ligands and siderophores. *Annual Review of Marine Science*, 1, 43–63. <https://doi.org/10.1146/annurev.marine.010908.163712>
- Wakabayashi, T., Ymamoto, A., Kazaana, A., Nakano, Y., Nojiri, Y., & Kashiwazaki, M. (2016). Antibacterial, Antifungal and Nematicidal Activities of Rare Earth Ions. *Biological Trace Element Research*, 174(2), 464–470. <https://doi.org/10.1007/s12011-016-0727-y>
- Wang, M. Q., & Xu, Z. R. (2003). Effect of supplemental lanthanum on the growth performance of pigs. *Asian-Australasian Journal of Animal Sciences*, 16(9), 1360–1363. <https://doi.org/10.5713/ajas.2003.1360>
- Wang, R., Clegg, J., Scott, P., Larkin, C., Deng, F., Thomas, A., et al. (2021). Reversible scavenging and advection – Resolving the neodymium paradox in the South Atlantic. *Geochimica et Cosmochimica Acta*, 314, 121–139. <https://doi.org/10.1016/j.gca.2021.09.015>
- Wang, S., Wu, S., Yan, W., Huang, W., Miao, L., Lu, J., et al. (2015). Rare metal elements in surface sediment from five bays on the northeastern coast of the South China Sea. *Environmental Earth Sciences*, 74(6), 4961–4971. <https://doi.org/10.1007/s12665-015-4504-6>
- Wang, Z. L., & Liu, C. Q. (2008). Geochemistry of rare earth elements in the dissolved, acid-soluble and residual phases in surface waters of the Changjiang Estuary. *Journal of Oceanography*, 64(3), 407–416. <https://doi.org/10.1007/s10872-008-0034-0>
- Wang, Z. L., Zhu, Z. Z., Wang, Z. L., & Liu, C. Q. (2013). Rare earth element geochemistry of waters and suspended particles in alkaline lakes using extraction and sequential chemical methods. *Geochemical Journal*, 47(6), 639–649. <https://doi.org/10.2343/geochemj.2.0290>
- Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59(7), 1217–1232. [https://doi.org/10.1016/0016-7037\(95\)00038-2](https://doi.org/10.1016/0016-7037(95)00038-2)
- Wei, B., Li, Y., Li, H., Yu, J., Ye, B., & Liang, T. (2013). Rare earth elements in human hair from a mining area of China. *Ecotoxicology and Environmental Safety*, 96, 118–123. <https://doi.org/10.1016/j.ecoenv.2013.05.031>
- Weis, J. S., & Weis, P. (2004). Metal uptake, transport and release by wetland plants: Implications for phytoremediation and restoration. *Environment International*, 30(5), 685–700. <https://doi.org/10.1016/j.envint.2003.11.002>
- Weltje, L., Heidenreich, H., Zhu, W., Wolterbeek, H. T., Korhammer, S., Goeij, J. J. M., & Markert, B. (2002). Lanthanide concentrations in freshwater plants and molluscs, related to those in surface water, pore water and sediment. A case study in The Netherlands. *Science of the Total Environment*, 286(1–3), 191–214. [https://doi.org/10.1016/S0048-9697\(01\)00978-0](https://doi.org/10.1016/S0048-9697(01)00978-0)
- Weltje, L., Verhoof, L. R. C. W., Verweij, W., & Hamers, T. (2004). Lutetium speciation and toxicity in a microbial bioassay: Testing the free-ion model for lanthanides. *Environmental Science and Technology*, 38(24), 6597–6604. <https://doi.org/10.1021/es049916m>
- Whitby, H., & van den Berg, C. M. G. (2015). Evidence for copper-binding humic substances in seawater. *Marine Chemistry*, 173, 282–290. <https://doi.org/10.1016/j.marchem.2014.09.011>
- Wilde, P., Quinby-Hunt, M. S., & Erdtmann, B.-D. (1996). The whole-rock cerium anomaly: A potential indicator of eustatic sea-level changes in shales of the anoxic facies. *Sedimentary Geology*, 101(1–2), 43–53. [https://doi.org/10.1016/0037-0738\(95\)00020-8](https://doi.org/10.1016/0037-0738(95)00020-8)
- Willis, S. S., & Johannesson, K. H. (2011). Controls on the geochemistry of rare earth elements in sediments and groundwaters of the Aquia aquifer, Maryland, USA. *Chemical Geology*, 285(1–4), 32–49. <https://doi.org/10.1016/j.chemgeo.2011.02.020>
- Wilson, D. J., Piotrowski, A. M., Galy, A., & Clegg, J. A. (2013). Reactivity of neodymium carriers in deep sea sediments: Implications for boundary exchange and paleoceanography. *Geochimica et Cosmochimica Acta*, 109, 197–221. <https://doi.org/10.1016/j.gca.2013.01.042>
- Wilson, D. J., Piotrowski, A. M., Galy, A., & McCave, I. N. (2012). A boundary exchange influence on deglacial neodymium isotope records from the deep western Indian Ocean. *Earth and Planetary Science Letters*, 341–344, 35–47. <https://doi.org/10.1016/j.epsl.2012.06.009>

- Wood, S. A. (1990a). The aqueous geochemistry of the rare-earth elements and yttrium. 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chemical Geology*, 82, 159–186. [https://doi.org/10.1016/0009-2541\(90\)90080-Q](https://doi.org/10.1016/0009-2541(90)90080-Q)
- Wood, S. A. (1990b). The aqueous geochemistry of the rare-earth elements and yttrium. 2. Theoretical predictions of speciation in hydrothermal solutions to 350°C at saturation water vapor pressure. *Chemical Geology*, 88(1–2), 99–125. [https://doi.org/10.1016/0009-2541\(90\)90106-H](https://doi.org/10.1016/0009-2541(90)90106-H)
- Wysocka, I. (2021). Determination of rare earth element concentrations in natural waters - A review of ICP-MS measurement approaches. *Talanta*, 221, 121636. <https://doi.org/10.1016/j.talanta.2020.121636>
- Xu, T., Zhang, M., Hu, J., Li, Z., Wu, T., Bao, J., et al. (2017). Behavioral deficits and neural damage of *Caenorhabditis elegans* induced by three rare earth elements. *Chemosphere*, 181, 55–62. <https://doi.org/10.1016/j.chemosphere.2017.04.068>
- Yoshida, T., Ozaki, T., Ohnuki, T., & Francis, A. J. (2004). Adsorption of rare earth elements by g-Al<sub>2</sub>O<sub>3</sub> and *Pseudomonas fluorescens* cells in the presence of desferrioxamine B: Implication of siderophores for the Ce anomaly. *Chemical Geology*, 212(3–4), 239–246. <https://doi.org/10.1016/j.chemgeo.2004.08.046>
- Yu, P., Hayes, S. A., O'Keefe, T. J., O'Keefe, M. J., & Stoffer, J. O. (2006). The phase stability of cerium species in aqueous systems. II. The Ce (III/IV)-H<sub>2</sub>O-H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub> systems. Equilibrium considerations and Pourbaix diagram calculations. *Journal of the Electrochemical Society*, 153(1), C74–C79. <https://doi.org/10.1149/1.2130572>
- Yuan, M., Guo, M.-N., Liu, W.-S., Liu, C., van der Ent, A., Morel, J. L., et al. (2017). The accumulation and fractionation of rare earth elements in hydroponically grown *Phytolacca americana* L. *Plant and Soil*, 421(1–2), 67–82. <https://doi.org/10.1007/s1104-017-3426-3>
- Yuksekdag, A., Kose-Mutlu, B., Siddiqui, A. F., Wiesner, M. R., & Koyuncu, I. (2022). A holistic approach for the recovery of rare earth elements and scandium from secondary sources under a circular economy framework – A review. *Chemosphere*, 293(October 2021), 133620. <https://doi.org/10.1016/j.chemosphere.2022.133620>
- Zaharescu, D. G., Burghilea, C. I., Dontsova, K., Presler, J. K., Maier, R. M., Huxman, T., et al. (2017). Ecosystem Composition Controls the Fate of Rare Earth Elements during Incipient Soil Genesis. *Scientific Reports*, 7, 1–15. <https://doi.org/10.1038/srep43208>
- Zapp, P., Schreiber, A., Marx, J., & Kuckshinrichs, W. (2022). Environmental impacts of rare earth production. *MRS Bulletin*, 47(3), 267–275. <https://doi.org/10.1557/s43577-022-00286-6>
- Zhang, C., Wang, L., Zhang, S., & Li, X. (1998). Geochemistry of rare earth elements in the mainstream of the Yangtze River, China. *Applied Geochemistry*, 13(4), 451–462. [https://doi.org/10.1016/S0883-2927\(97\)00079-6](https://doi.org/10.1016/S0883-2927(97)00079-6)
- Zhang, H., He, X., Bai, W., Guo, X., Zhang, Z., Chaia, Z., & Zhao, Y. (2010). Ecotoxicological assessment of lanthanum with *Caenorhabditis elegans* in liquid medium. *Metallomics*, 2(12), 806–810. <https://doi.org/10.1039/c0mt00059k>
- Zhang, K., & Shields, G. A. (2022). Sedimentary Ce anomalies: Secular change and implications for paleoenvironmental evolution. *Earth-Science Reviews*, 229, 104015. <https://doi.org/10.1016/j.earscirev.2022.104015>
- Zhang, R., Yan, C., & Liu, J. (2013). Effect of Mangroves on the Horizontal and Vertical Distributions of Rare Earth Elements in Sediments of the Zhangjiang Estuary in Fujian Province, Southeastern China. *Journal of Coastal Research*, 29(2005), 1341–1350. <https://doi.org/10.2112/JCOASTRES-D-11-00215.1>
- Zhang, X., Hu, Z., Pan, H., Bai, Y., Hu, Y., & Jin, S. (2022). Effects of rare earth elements on bacteria in rhizosphere, root, phyllosphere and leaf of soil-rice ecosystem. *Scientific Reports*, 12(1), 1–17. <https://doi.org/10.1038/s41598-022-06003-2>
- Zhao, P., Bi, R., Sanganyado, E., Zeng, X., Li, W., Lyu, Z., et al. (2022). Rare earth elements in oysters and mussels collected from the Chinese coast: Bioaccumulation and human health risks. *Marine Pollution Bulletin*, 184(July), 114127. <https://doi.org/10.1016/j.marpolbul.2022.114127>
- Zhao, Y., Wei, W., Li, S., Yang, T., Zhang, R., Somerville, I., et al. (2021). Rare earth element geochemistry of carbonates as a proxy for deep-time environmental reconstruction. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 574, 110443. <https://doi.org/10.1016/j.palaeo.2021.110443>
- Zheng, H., Yang, Y., Liu, W., Zhong, Y., Cao, Y., Qiu, R. L., et al. (2023). Rare earth elements detoxification mechanism in the hyperaccumulator *Dicranopteris linearis*: [silicon-pectin] matrix fixation. *Journal of Hazardous Materials*, 452(November 2022), 131254. <https://doi.org/10.1016/j.jhazmat.2023.131254>
- Zheng, X. Y., Plancherel, Y., Saito, M. A., Scott, P. M., & Henderson, G. M. (2016). Rare earth elements (REEs) in the tropical South Atlantic and quantitative deconvolution of their non-conservative behavior. *Geochimica et Cosmochimica Acta*, 177, 217–237. <https://doi.org/10.1016/j.gca.2016.01.018>
- Zhou, B., Li, Z., Zhao, Y., Zhang, C., & Wei, Y. (2016). Rare earth elements supply vs. clean energy technologies: New problems to be solve. *Mineral Resources Management*, 32(4), 29–44. <https://doi.org/10.1515/gospo-2016-0039>
- Zhou, J. L., Rowland, S., Fauzi, R., Mantoura, C., & Braven, J. (1994). The formation of humic coatings on mineral particles under simulated estuarine conditions—A mechanistic study. *Water Research*, 28(3), 571–579. [https://doi.org/10.1016/0043-1354\(94\)90008-6](https://doi.org/10.1016/0043-1354(94)90008-6)
- Zocher, A. L., Klimpel, F., Kraemer, D., & Bau, M. (2022). Naturally grown duckweeds as quasi-hyperaccumulators of rare earth elements and yttrium in aquatic systems and the bioavailability of gadolinium-based MRI contrast agents. *Science of the Total Environment*, 838(5), 155909. <https://doi.org/10.1016/j.scitotenv.2022.155909>
- Zocher, A. L., Kraemer, D., Merschel, G., & Bau, M. (2018). Distribution of major and trace elements in the bolete mushroom *Suillus luteus* and the bioavailability of rare earth elements. *Chemical Geology*, 483(2), 491–500. <https://doi.org/10.1016/j.chemgeo.2018.03.019>
- Zoll, A. M., & Schijf, J. (2012). A surface complexation model of YREE sorption on *Ulva lactuca* in 0.05–5.0M NaCl solutions. *Geochimica et Cosmochimica Acta*, 97, 183–199. <https://doi.org/10.1016/j.gca.2012.08.022>
- Zwicker, J., Smrzka, D., Vadillo, I., Jiménez-Gavilán, P., Giampouras, M., Peckmann, J., & Bach, W. (2022). Trace and rare earth element distribution in hyperalkaline serpentinite-hosted spring waters and associated authigenic carbonates from the Ronda peridotite. *Applied Geochemistry*, 147(June), 105492. <https://doi.org/10.1016/j.apgeochem.2022.105492>