



HAL
open science

Relationship between the distribution of rare earth elements in soil pools with plant uptake: a sequential extraction study

Kaisa Forsyth, Aline Dia, Rosa Marques, Maria Isabel Prudêncio, Cynthia Obregón-Castro, Catarina Diamantino, Edgar Carvalho, Maxime Pattier, Mélanie Davranche, Mathieu Pédrot

► **To cite this version:**

Kaisa Forsyth, Aline Dia, Rosa Marques, Maria Isabel Prudêncio, Cynthia Obregón-Castro, et al.. Relationship between the distribution of rare earth elements in soil pools with plant uptake: a sequential extraction study. *Plant and Soil*, 2025, 512, pp.1137-1152. <10.1007/s11104-024-07135-2>. <insu-04866127>

HAL Id: insu-04866127

<https://insu.hal.science/insu-04866127v1>

Submitted on 6 Jan 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY 4.0 - Attribution - International License



Relationship between the distribution of rare earth elements in soil pools with plant uptake: a sequential extraction study

Kaisa Forsyth · Aline Dia · Rosa Marques · Maria Isabel Prudêncio ·
Cynthia Obregón-Castro · Catarina Diamantino · Edgar Carvalho ·
Maxime Pattier · Mélanie Davranche · Mathieu Pédrot

Received: 26 July 2024 / Accepted: 4 December 2024
© The Author(s) 2024

Abstract

Background and Aims Many studies have considered whether all forms of rare earth elements (REEs) in the soil are potentially bioavailable. The general consensus is that the exchangeable and carbonate-bound mineral pool is bioavailable. However, within the rhizosphere, site-specific geochemical conditions and biological weathering (due to plants, animals and

microbes) may cause insoluble pools of REEs in the soil to become plant bioavailable.

Methods This study categorized soil into four fractions using the Community Bureau of Reference (BCR) sequential extraction method. The geochemical associations of REEs with soil fractions were assessed to determine which mineral and organic pools were most bioavailable by comparing the similarity of REE fractionation patterns in local plant tissues with the BCR extraction results for compatible soils.

Results The results showed that the residual or more recalcitrant fraction of the soil displays a convex REE pattern with distinct depletion of middle REEs (MREEs) compared with light REEs (LREEs) and heavy REEs (HREEs). Some evidence suggested that Eu may be excluded by plants, as anomalous Eu concentrations were observed when the belowground plant tissue concentrations were normalized to the BCR extraction data.

Conclusions This study demonstrates that the REEs in belowground plant tissue are closely related, not only to exchangeable and carbonate-bound phases, but also to reducible and oxidizable soil fractions. According to the REE patterns, MREEs are more mobile than LREEs and HREEs, indicating enhanced bioavailability of MREEs.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11104-024-07135-2>.

Responsible Editor: Antony Van der Ent.

K. Forsyth (✉) · A. Dia · M. Pattier · M. Davranche ·
M. Pédrot
Géosciences Rennes, UMR 6118 CNRS, Univ. Rennes,
Rennes 35000, France
e-mail: kaisa.forsyth@gmail.com

R. Marques · M. I. Prudêncio · C. Obregón-Castro
Centro de Ciências e Tecnologias Nucleares,
Instituto Superior Técnico, Universidade de Lisboa,
Bobadela 2695-066, Portugal

R. Marques · M. I. Prudêncio
Departamento de Engenharia e Ciências Nucleares
(DECN), Instituto Superior Técnico, Universidade de
Lisboa, Bobadela 2695-066, Portugal

C. Diamantino · E. Carvalho
EDM - Empresa de Desenvolvimento Mineiro, S.A.,
Lisboa 1070-050, Portugal

Keywords Sequential extraction · Rare Earth elements · Plant · Soil · Water · Bioaccumulation

Introduction

Rare earth elements (REEs) are technology-critical elements (Van Gosen et al. 2017). Increasing evidence of their toxicity and prevalence in the biosphere indicates that they pose a risk to human and environmental health (Gong et al. 2021; Li et al. 2013; Merschel and Bau 1995; Pagano et al. 2015; Rim et al. 2013; Wakabayashi et al. 2016). These 14 elements of the lanthanide series typically adapt to a +3 oxidation state, with the exception of Ce, which can be oxidized to +4 and Eu, which can be reduced to +2. Another common attribute is the filling of the 4f electron shell, which results in insufficient shielding of the nucleus and ultimately a contraction of the atomic radius. Due to this lanthanide contraction phenomenon, REEs are accepted in isomorphic substitution with similarly sized elements such as Ca (Shannon 1976). Minor differences in how these elements interact with surfaces and compatible ligands contribute to their partitioning and fractionation behavior in the soil. It is therefore convenient to categorize REEs as light REEs (LREEs) (La to Nd), middle REEs (MREEs) (Sm to Tb), and heavy REEs (HREEs) (Dy to Lu).

As lithophilic elements, REEs typically have limited solubility. Exceptions to this trend are found in environmental conditions where a low pH develops and metal solubility increases (Baker et al. 1990; Pérez-López et al. 2010; Prudêncio et al. 2015; Soyol-Erdene et al. 2018). The contributions of different mineral pools to total REEs in the soil are described in Migaszewski and Gałuszka (2015), who estimated that 43% of all REEs are associated with silicate minerals, 23% with carbonates, 14% with oxides, and 14% with phosphates and oxyhydroxides. Although the contribution of REEs from soil organic matter was not quantified by Migaszewski and Gałuszka (2015), other studies have shown that the organic pool contributes between 1.84 and 26.5% of the REEs in soil (Pang et al. 2002).

Given that these complex biogeochemical interactions dictate the bioavailability of not only REEs, but all elements in rhizosphere, predicting the origin of elements found in plants is a challenge. Brioschi et al. (2013) theorized that the preferential uptake of LREEs can be summarized as follows: (1) preferential precipitation of HREEs over LREEs into Fe-oxyhydroxide minerals (suggesting that Fe-oxyhydroxide mineral-associated fraction is fixed and generally not

bioavailable) and (2) preferential uptake of free and non-complexed cations (LREEs) by plants. Although there is a general consensus that the dissolved pool and easily exchangeable cations are bioavailable and pose the greatest threat to local ecology (Liang et al. 2005; Pérez-López et al. 2008), this pool is often minimal in comparison with the sum of elements found in plant tissue (Liang et al. 2005).

A possible explanation for this disparity is that plants affect nutrient solubility and further weather the surrounding soil matrix (Stille et al. 2006) by altering pH and redox potential and producing biogenic exudates (Liang et al. 2008; Wyttenbach et al. 1998b). Manipulation of rhizosphere conditions can even extend outside the plant, with symbiotic microbes playing a major role in nutrient extraction and limiting the impacts of metal toxicity for plants (Kong and Glick 2017; Sessitsch et al. 2013). In particular, the literature describing the solubilization of REEs by low-molecular-weight organic acids (LMWOA) and humic/fulvic acids (Dia et al. 2000; Pourret et al. 2007; Tang and Johannesson 2003; Tyler 2004; Wiche and Pourret 2023) suggests that the bioavailable pool should be expanded to include REEs associated with other pools of soil minerals and organic matter, which are classically considered less labile.

The Community Bureau of Reference (BCR) sequential extraction is typically used for environmental risk assessment and for predicting the origin and fate of polyvalent cations in soil (Ure et al. 1993). Selective partitioning of the soil enables the identification of metals associated with the (1) exchangeable and carbonate-bound, (2) oxidizable, (3) reducible, and (4) residual soil fractions. Knowledge of the distribution of REEs within these phases provides insight into their behavior and fate. Many studies have attempted to use BCR and other soil extraction methods to predict the toxicity and bioavailability of REEs and other trace metal contaminants (Kubová et al. 2008; Liang et al. 2005; Pang et al. 2002; Shan et al. 2003; Wang et al. 2001a, b; Wyttenbach et al. 1998a; Zhang and Shan 2001). Kubová et al. (2008) used BCR extraction to compare the bioavailability of nine different elements in plants. Ultimately, they concluded that the results of sequential extraction alone are not a pertinent predictor of bioavailability, but this method could be used to qualitatively determine the relative amounts of plant-available elements.

Although the geochemical fractionation of REEs is not a good predictor of bioavailability on its own, this approach can be used to predict which soil REE fractions are vulnerable to solubilization. Solubility is a major barrier to bioavailability in the rhizosphere, thus this potentially soluble pool can approximate a bioavailable pool. Based on previous studies, REEs are likely geochemically partitioned before entering plant tissues (Brioschi et al. 2013; Forsyth et al. 2023; Gonzalez et al. 2014; Tyler 2004). Rare earth elements are a physicochemically uniform group of elements that should undergo similar biogeochemical reactions (Gonzalez et al. 2014). Slight differences in their interactions with compatible ligands, their redox chemistries, and their atomic radii lead to the fractionation of individual elements into different soil phases. Therefore, a sequential extraction scheme can be useful to compare the lability and recalcitrance of different REEs against each other. This information can then be used to determine which elements exhibit the highest potential for phytoavailability and the conditions that promote this.

The current literature relating REE chemical fractionation within soils to plant phytoavailability is limited. Many studies have quantified only a subset of REEs, instead of the entire series (Shan et al. 2003; Wang et al. 2001b; Wyttenbach et al. 1998b; Xinde et al. 2000; Zhang and Shan 2001), and often, these studies focus on aboveground plant tissue rather than belowground tissue (Wang et al. 2001b; Wyttenbach et al. 1998b; Xinde et al. 2000). However, the biological partitioning of REEs from belowground to aboveground tissues has been well documented (Forsyth et al. 2023; Liang et al. 2008; Tyler 2004). The partitioning of REEs into aboveground tissue, while not observed across all specimens, seems to be related to plant species endogeneity rather than the bioavailability of the REEs (Liang et al. 2008; Tyler 2004). For this reason, the current study focuses on relating the chemical fractionation of REEs in soils to the REE contents in belowground tissue rather than aboveground tissue, with further studies planned to assess the mechanisms and effects of biological partitioning of REEs in plants.

This study uses a BCR sequential extraction scheme to investigate the sources of REEs in plant tissues collected from three distinct legacy mining sites in Portugal. Study sites were selected based on their geochemical background. Generally, the

environmental conditions of these sites promote the dissolution of polyvalent cation-bearing minerals. As REEs are ubiquitous elements in the Earth's crust (Taylor and McLennan 1985), incidental release of geogenic REEs can be promoted by the Acid Mine Drainage (AMD) conditions formed in mining sites, like those selected (Ferreira da Silva et al. 2009; Pérez-López et al. 2010; Prudêncio et al. 2015; Soyol-Erdene et al. 2018). Many studies having demonstrated that REE solubility is high in such areas (Grawunder et al. 2014; Pérez-López et al. 2010). Soils and sediments sequentially extracted in this experiment correspond to samples reported by Forsyth et al. (2023), which published a survey of total REE concentrations in water, soil, and plant samples from the three legacy mining sites selected for this study. The BCR sequential extractions are contextualized using the total concentration of REE in plants and soils/sediments presented in Forsyth et al. (2023).

Materials and methods

Site description

Samples were collected in November 2020 from three mining sites: Lousal, São Domingos, and Quinta do Bispo (Portugal). A detailed description of the sample collection and processing procedures can be found in Forsyth et al. (2023), which presents a comprehensive survey of the concentrations of REEs and their associations in surface waters, soils/sediments, and belowground and aboveground plant tissues. The following section details the current knowledge on the mineralogy of these sites and describes the procedures used to determine the chemical fractionation of soils/sediments.

Lousal

Lousal mining operations occurred along the Sado Valley Fault, an area of volcanic deposition with major hydrothermal alteration (Morais et al. 2020) that resulted in volcanic sedimentary complexes (VSCs) emblematic of the Iberian Pyrite Belt (IPB). The area features bimodal volcanic rocks with massive sulfide lenses (predominantly composed of pyrite with lesser amounts of chalcopyrite, galena, sphalerite, pyrrhotite, marcasite, bournonite, tetrahedrite,

arsenopyrite, cobaltite, magnetite, and gold; Luís et al. 2011) and carbonate veins. Mantle melting is assumed to be responsible for the characteristic enrichment of Eu and Tb and the depletion of Sc, Al, and Ti in the felsic and intermediate geology (Morais et al. 2020). Devonian shales and quartzites from the Corona Formation (Luís et al. 2011; Matos et al. 2014) and other post-Mesozoic materials overlie a Paleozoic basement (Oliveira et al. 2001) in the area surrounding the mine's passive treatment system. This treatment system is located near the confined waste piles, which produces AMD, and successfully treats effluents for sulfates, arsenic, aluminum, iron, copper, and chromium before confluence with the nearby Corona River (Empresa de Desenvolvimento Mineiro [EDM] and Direcção Geral de Energia e Geologia [DGEG], 2011). Metal-enriched effluents progress through the 17-basin treatment system, where the pH slowly increases along the reach, causing the precipitation of secondary minerals with further stabilization of metals supported by the aerobic wetland system. Lousal was the only study site that contained a passive treatment system for AMD effluent in the sampling period.

Two aquatic sediment samples were collected from the Lousal site: L-01, which corresponds to sediment collected from a stock pond outside the mining area, i.e. in the fresh water from the Albufeira da Barragem da Tapada reservoir; and L-02, which is aquatic sediment collected from the 6th treatment basin, where the aerobic wetland basins begin.

São Domingos

Similar to Lousal, São Domingos is hosted in the IPB of southern Portugal. The exploitation of iron-sulfide ores along with copper, lead, zinc, and sulfur over time has led to the continual generation of AMD at this site (Álvarez-Valero et al. 2008). Although the dominant ore composition is pyrite, with heterogeneous arrangements of chalcopyrite, galena, and sphalerite (Durães et al. 2017), long-term usage of this site has led to the development of many secondary minerals along the São Domingos river valley. Secondary minerals are typically formed from the supersaturation of various metal species associated with AMD. They include Fe-oxide gossans (goethite and hematite) along with sulfate salts such as alunogens, as well as calcite, clinocllore, gypsum, jarosite, and

schwertmannite (Durães et al. 2017; Ferreira et al. 2021). Much of the mining waste materials have been characterized previously by Álvarez-Valero et al. (2008), who focus on the mineralogical and chemical composition, and Pérez-López et al. (2008), who performed a sequential extraction on the materials characterized by Álvarez-Valero et al. (2008) to identify the risks posed by various trace and major elements. Neither paper described the REE contents.

Three soil samples were collected from the São Domingos River Valley: SD-01, SD-02, and SD-03. The soil corresponding to SD-01 was retrieved from outside the mining area, close to the Albufeira da Tapada Grande dam. The soil around this reservoir represents the background lithology (Quental et al. 2002) and is weathered from shales of the Represa Formation, felsic and mafic volcanic rocks, and black shales (Pereira et al. 2008). Soils SD-02 and SD-03 were collected along the São Domingos river valley in areas previously identified by Pérez-López et al. (2008) as being landfilled with heavily siliceous and inert material. Despite the use of a relatively inert material (up to 90% quartz according to Pérez-López et al. 2008), vegetation in the area is still sparse, presumably due to the presence of secondary precipitates on the soil surface after runoff (Ferreira et al. 2021).

Quinta do Bispo

Unlike São Domingos and Lousal, Quinta do Bispo is hosted in Variscan granites and pre-Cambrian metasediments (Ramalho et al. 2009). Previous studies have characterized the granitic rocks of Quinta do Bispo as (1) coarse-grained, (2) medium-grained, and (3) medium-fine-grained monzonitic two-mica granites (Matos-Dias and Costa 1972; Barbosa 2012 and references therein). Deposits of uranium oxides and uranium phosphates are associated with hydrothermal deposition into stockworks (Barbosa 2012). Metasomatic albitization of feldspars and chloritization of biotite are evident in cores taken from the area (Barbosa 2012). Previous studies of the area have attributed Eu anomalies to the albitization of plagioclase minerals (Cardenas et al. 2023; Forsyth et al. 2023), where Ca^{2+} and Eu^{2+} incorporated in plagioclases are metasomatically displaced, resulting in positive

Eu anomalies corresponding to uranium ores and negative Eu anomalies corresponding to the altered material.

Although manganese oxides, pyrite, and arsenopyrite have been associated with the mineralogy of Quinta do Bispo, the dominant ore mineralogy comprises autunite and torbernite (Cardenas et al. 2023). Uranium was extracted from these ores between 1979 and 1987. The original ores were exploited at the Quinta do Bispo site and processed in Urgeiriça (Pereira et al. 2014). However, after 1992, the open pit at Quinta do Bispo was used for in situ leaching (ISL) of low-grade ores; thus, the site is impacted by acidic wastewaters that are isolated in an open pit awaiting treatment.

Seven soil samples corresponding to three distinct geological units were collected from the Quinta do Bispo site. Samples QB-01 and QB-01b represent soils collected from outside the mining area, with similarly medium-grain granite as in mining area. Samples QB-02 and QB-02b represent a large waste rock pile on site and thus should reflect uranium enrichment consistent with the exploited material. Samples QB-03, QB-04, and QB-04b correspond to the alluvium formed by an ephemeral stream, reflecting weathering from materials in the surrounding drainage basin. Samples QB-01b, QB-02b, and QB-04b are distinct from the other samples collected at Quinta do Bispo because they represent bulk material that was not collected from a plant rhizosphere. These samples were collected to compare the rhizosphere environment to that of the bulk soil.

BCR extraction procedure

Chemical fractionation was determined using the standard three-step BCR extraction scheme established by the Standard Measurements and Testing Program of the European Community (Ure et al. 1993). BCR extraction partitions soil into three fractions defined as the “easily exchangeable and carbonate-bound” (exchangeable), “reducible mineral” (reducible), and “oxidizable mineral and organic matter” (oxidizable) soil fractions. The soil fraction that remains can then be calculated using Eq. 1, where the sum of the elements associated with the three sequential extraction fractions is subtracted from the total concentration of elements in the soil to determine the remaining amounts, including

REEs, in the residual fraction, which corresponds to a more recalcitrant pool of REEs.

$$\text{REE}_{\text{Resid.}} = \text{REE}_{\text{soil/aquatic sediment}} - (\text{REE}_{\text{exchangeable}} + \text{REE}_{\text{reducible}} + \text{REE}_{\text{oxidizable}}) \quad (1)$$

All materials were prepared in a clean room and decontaminated using nitric acid (1.5 M HNO₃) washing for 24 h at 45 °C, followed by 24 h washing with ultrapure water (18 MΩ-cm) at 45 °C. Approximately 0.5 g of soil was added to a decontaminated 50 mL centrifuge tube, with the reagents and agitation times are reported in Table 1. The supernatant resulting from each extraction step was separated by centrifugation and filtered through a 0.2 μm polyethersulfone (PES) filter before analysis. Carbon from the reagents used in each of the sequential extraction steps was digested in preparation for inductively coupled plasma–mass spectrometry (ICP–MS) analysis. Concentrated HNO₃ was used to digest the carbon associated with the “exchangeable and carbonate-bound” and “oxidizable minerals and organic material” extracts, while a combination of HCl and HNO₃ was used to digest the carbon in the “reducible mineral” extracts.

Plant tissue data

The soils studied by sequential extraction were collected as part of a campaign to catalog REE concentrations in plants, soils, sediments, and waters of mining sites. A large amount of background information pertaining to these samples is published in Forsyth

Table 1 Modified sequential extraction procedure (Ure et al. 1993)

Target Fraction	Reagent	Time
BCR 1: exchangeable	40 mL of 0.11 M acetic acid solution	16 h
BCR 2: reducible	40 mL of 0.5 M hydroxylamine hydrochloride adjusted to pH 1.5	16 h
BCR 3: oxidizable	Predigestion at 85 °C using 20 mL 8.8 M hydrogen peroxide 50 mL of 1 M ammonium acetate adjusted to pH 2	N/A 16 h

*N/A indicates a time that was determined by the rate of sediment digestion and was not confined to any particular time window

et al. (2023). The soils tested matched to plant samples, which included the species: *Cistus ladanifer*, *Typha latifolia*, *Juncus acutus*, *Pteridium aquilinum*, *Retama sphaerocarpa*, and *Salix sp.* Biota varied among sites, none of the plants grew in all three collection sites. Plants were collected from within a 1 m grid in the locations detailed in each site description. For this study only the belowground plant tissue data was used to determine the uptake of REE from BCR fractions, aboveground tissue was excluded as partitioning of REE occurs between uptake and assimilation into aboveground tissues. The belowground tissue mass includes: roots, rhizomes, and any transition material from roots to stem that were beneath the soil. Belowground tissue was processed using multiple washes with deionized water (18 M Ω -cm) followed by drying at 50 °C in an oven for 4 days and grinding using a zircon ball-mill. Belowground plant samples were then digested using a microwave (Anton Paar Multiwave 7000) digestion method. Tomato leaves standard 1573a (NIST[®] SRM[®]) was used as a reference material and digestions were performed in triplicate. Though there is no certified reference values for REEs in 1573a NIST, there are values without approximated errors reported for La, Ce, Gd, and Sm. Recovery rates for the reported REE were within 17% and all of the REE concentrations recorded for the triplicates were within 5% of each other.

Rare earth element analysis

The REE concentrations in the sequential extraction solutions and digestions were measured using a quadrupole ICP-MS (Agilent Technologies 7700 \times). The matrix of each sequential extract was acidified to match a 0.37 M HNO₃ concentration. The instrument was tuned to account for oxide and double-charged ion formation, normal plasma conditions were used (no gas mode). The concentrations were determined using a conventional 7-point external calibration procedure using multielemental solutions acidified in a 0.37 M HNO₃ matrix with online introduction of a Rh internal standard. Rhodium was introduced to correct for instrumental drift and possible matrix effects. The international geostandard SLRS-6 was used to check the validity and reproducibility of the results (Yéghicheyan et al. 2019). The typical uncertainties, including all error sources, were below $\pm 5\%$ for all the REEs.

The detection limits were calculated following the AFNOR protocol, and values of <0.25 ppt (ng L⁻¹) were obtained for all REEs. Interference from Ba-oxides and REE-oxides were accounted for using the methods reported in Aries et al. (2000), and corrections were applied to REEs with a mass greater than that of Sm. The above procedures are standard in analyses at the University of Rennes analytical platform, and similar protocols were employed by Davranche et al. (2004), Pédrot et al. (2009), and Forsyth et al. (2023) to obtain REE concentrations in waters, soils, sediments, and plant tissues.

Elements were categorized as LREEs (La-Pm), MREEs (Sm-Tb), and HREEs (Dy-Lu). Since both Ce and Eu can exhibit fractionation and anomalous concentrations due to their additional oxidation states, their behavior was described using linear extrapolation of the soil-normalized REE data (Eqs. 2 and 3, respectively), where Ce/Ce* represents the cerium anomaly and Eu/Eu* represents the europium anomaly; the greater this value varies from 1, the more anomalous the concentration is.

$$Ce/Ce^* = \frac{2(Ce)}{La + Pr} \quad (2)$$

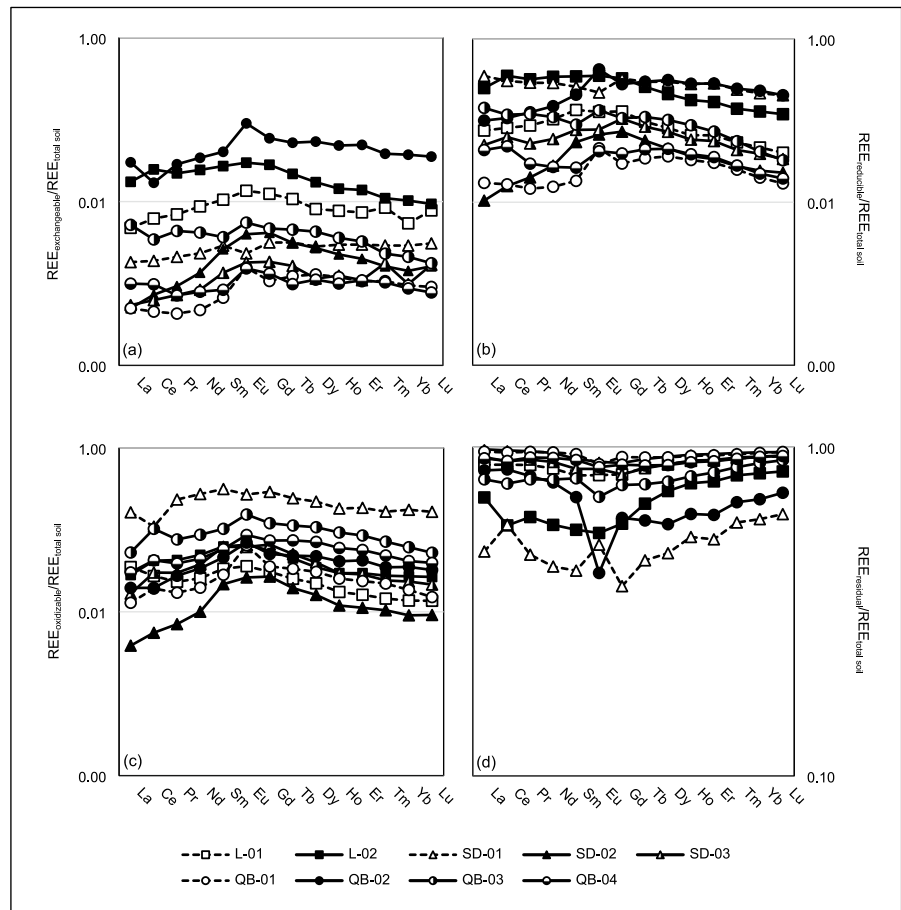
$$Eu/Eu^* = \frac{2(Eu)}{Sm + Gd} \quad (3)$$

Results

REE fractionation in legacy mining sites

The concentration in $\mu\text{g kg}^{-1}$ of the REE associated with each BCR fraction can be found in Table S1 of the supplementary materials. The REE fractionation, expressed as a percentage of the total soil REEs, is shown in Table S2 which is provided in the supplementary materials. Figure 1a and c demonstrate the REE fractionation for each soil sample (the data are normalized to the total soil REEs and are plotted on a log scale). These figures can be used to interpret the fractionation of individual REEs in soil. For all samples, the majority of the REEs are associated with the residual fraction, demonstrating the relatively recalcitrant and conservative behavior

Fig. 1 Log-scale plots of the relative REE contents of individual REEs in the (a) exchangeable (b) reducible, and (c) oxidizable fractions after normalization to the total soil/sediment content. Plot (d) expresses the contents of REEs in the residual fraction as percentages and is not log scaled. Dashed lines correspond to samples taken from outside the mining areas. Samples from São Domingos are indicated by triangles, samples from Quinta do Bispo are indicated by circles, and samples from Lousal are indicated by squares



of these elements. Middle REEs are enriched in the exchangeable (Fig. 1a), reducible (Fig. 1b), and oxidizable (Fig. 1c) soil fractions. This enrichment is complemented by the slight depletion of MREEs plotted in Fig. 1d, which plots the soil-normalized residual REE content.

Lousal

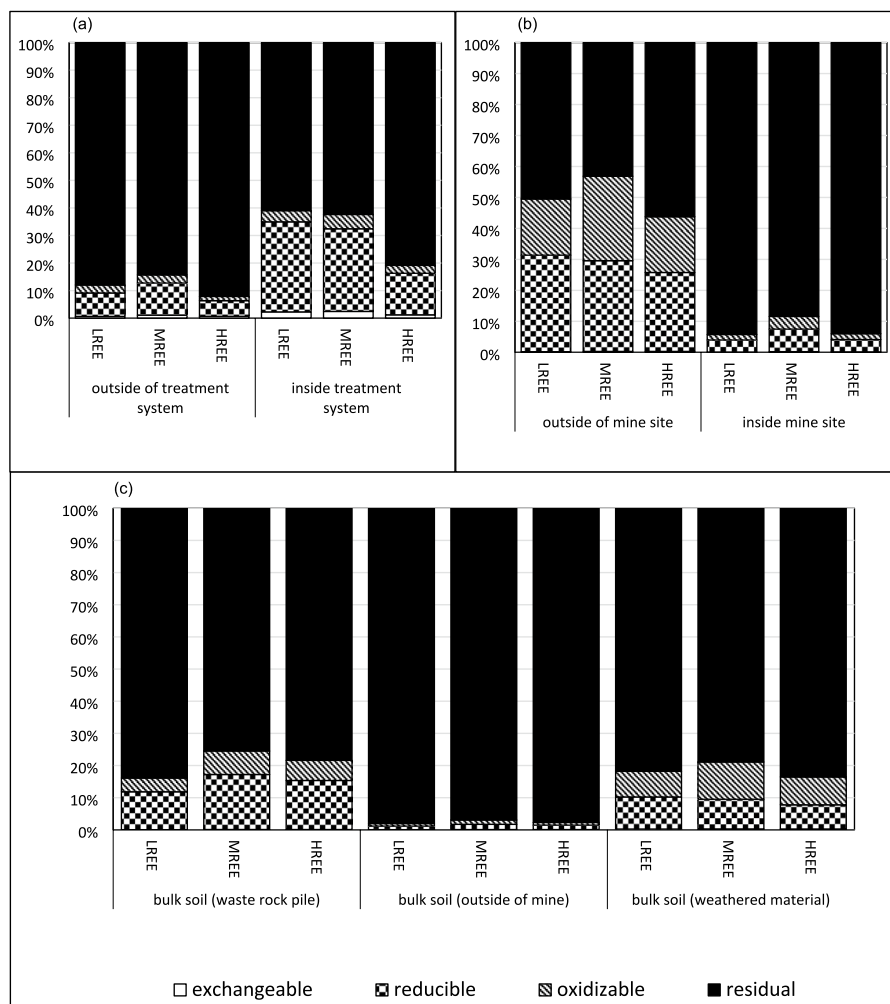
Figure 2a displays the contents of REEs associated with sediments collected from inside and outside the passive treatment system at Lousal. The aquatic sediment collected from Lousal had the least amount of REEs associated with the residual fraction. The fractionation of REEs was compared between sediment samples collected from outside the treatment system and inside the treatment system. The results verified that the processes inside the treatment system modified the initial sediment profile; LREEs were preferentially incorporated into the exchangeable,

reducible, and oxidizable fractions of the sediments collected from inside the treatment basin. This trend is most notable in the reducible phase, in which the LREE content increased from 9% outside to 33% inside the treatment system. The exchangeable, reducible, and oxidizable fractions also exhibited a slightly positive Ce/Ce^* , ranging from 1.19 to 1.29, which was accompanied by a slightly negative Ce/Ce^* in the residual fraction (0.88).

São Domingos

Similar to Lousal, the residual fraction accounted for the largest REE pool (Fig. 2b). Again, there was significant variation in the REE-bearing soil fractions outside and inside the mining area. The percentage of REEs associated with the reducible and oxidizable phases was greater in the samples collected outside the mining area than in the samples collected inside the mining area. Soil samples collected from São

Fig. 2 REE fractionation in samples collected (a) inside and outside the Lousal passive treatment system, (b) inside and outside the São Domingos River Valley, and (c) from a tailing pile, outside the mine, and weathered material near the mine at Quinta do Bispo



Domingos river valley exhibited similar REE fractionation across all the BCR steps, with a skewed concave pattern of MREE > HREE > LREE. This finding contrasted to the samples collected outside the mining area, which displayed MREE enrichment in the oxidizable soil fraction, but a LREE > MREE > HREE pattern in the reducible fraction was verified.

For samples collected outside the mining area, Ce/Ce* and Eu/Eu* seemed to be predominantly related to the residual soil fraction (Fig. 1), which showed enrichment of Ce (Ce/Ce*=1.22) and Eu (Eu/Eu*=1.26) relative to their total contents in the soil. Slightly negative Eu/Eu* values were associated with the exchangeable, reducible, and oxidizable BCR fractions. Cerium was depleted in the oxidizable fraction, which had a significantly negative Ce/Ce* of 0.55. The soil sample collected in the mining area

showed positive Ce/Ce*, associated with both reducible and oxidizable solid phases.

Quinta do Bispo

Samples were collected from three distinct soil environments at the Quinta do Bispo site: a low-grade ore pile, weathered materials collected in an ephemeral stream below Quinta do Bispo, and the surrounding lithology outside the mining area (for comparison). Figure 2c displays the distributions of LREEs, MREEs, and HREEs in the bulk soil collected from these three different sampling points. Although the total concentrations of LREEs, MREEs, and HREEs in the soils collected from Quinta do Bispo were not significantly different (Forsyth et al. 2023), the geochemical associations of these REE groups

varied among the three sampling points. As mentioned before, the surrounding area is a granite with metasomatic deposits of uranium. The sample collected from outside the mining area appears to reflect the surrounding lithology, with the residual fraction accounting for 89–98% of the REEs. Across all Quinta do Bispo sites, the residual fraction contained the largest proportion of REEs. The samples collected from the alluvium and the waste rock pile contained similar proportions of residual REEs. However, the alluvium contained a lower proportion of REEs associated with the reducible fraction when compared to the waste rock pile (9% instead of 15%) and a slightly higher relative proportion of oxidizable REEs (9%, instead of 6%).

Strong positive Eu/Eu^* values were observed in all of the Quinta do Bispo soils throughout all sequential extraction steps, showing that Eu^{2+} is preferentially assimilated into more labile minerals rather than the recalcitrant residual fraction. However, because the residual fraction represents such a large pool of REEs, the soils collected from the area surrounding the ore body have a net negative Eu/Eu^* (Forsyth et al. 2023); samples collected from QB-02 and QB-02b, which resemble the ore body, were enriched in hydrothermally deposited Eu.

REE fractionation influenced by plants

Bulk and rhizosphere soils at Quinta do Bispo were compared. For both the bulk and rhizosphere soils, the residual fraction was the dominant fraction, accounting for 62–98% of individual REEs. Forsyth et al. (2023) reported no significant differences among rhizosphere and bulk soil REE concentrations. However, the BCR extraction results in the current study showed slight differences between the rhizosphere and bulk soil fractions, as displayed in Fig. 3. The rhizosphere samples showed a 0.77–1.94% increase in the amount of REEs associated with the exchangeable fraction; this increase corresponded to a $1.69 \mu\text{g kg}^{-1}$ increase in the total soil REE concentration in relation to bulk soil. Since the exchangeable fraction represents such a small proportion of soil REE, this increase is not very significant. An increase of 4.02% and 4.24% in the reducible fraction were observed for MREEs and HREEs, respectively. However, the amount of LREEs associated with the reducible fraction increased by only 0.12%, which corresponded to

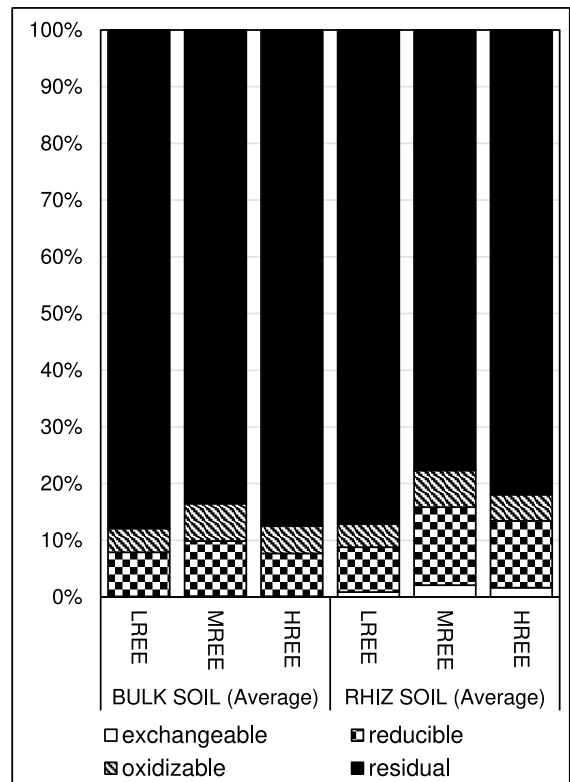


Fig. 3 REE fractionation in rhizosphere soils (Rhiz. soil) and bulk soils collected from Quinta do Bispo

$0.28 \mu\text{g kg}^{-1}$ increase in total rhizosphere soil REE concentrations.

When the REE concentrations in the belowground plant tissues (REE_{BG}) were normalized to the BCR extraction data for soils and sediments collected from the rhizosphere (Fig. 4a and d), the patterns were relatively smooth, and negative Eu/Eu^* values were identified in samples from Quinta do Bispo. This finding, paired with the positive Eu/Eu^* in Fig. 1a and d, demonstrates that the mobility of Eu in these soils was high, but that the plant uptake of Eu was relatively low.

Discussion

Influence of mining conditions in REE fractionation

Pang et al. (2002) reported that the average amount of REEs associated with the residual soil fraction was between 45.2% and 94.7%, and many authors

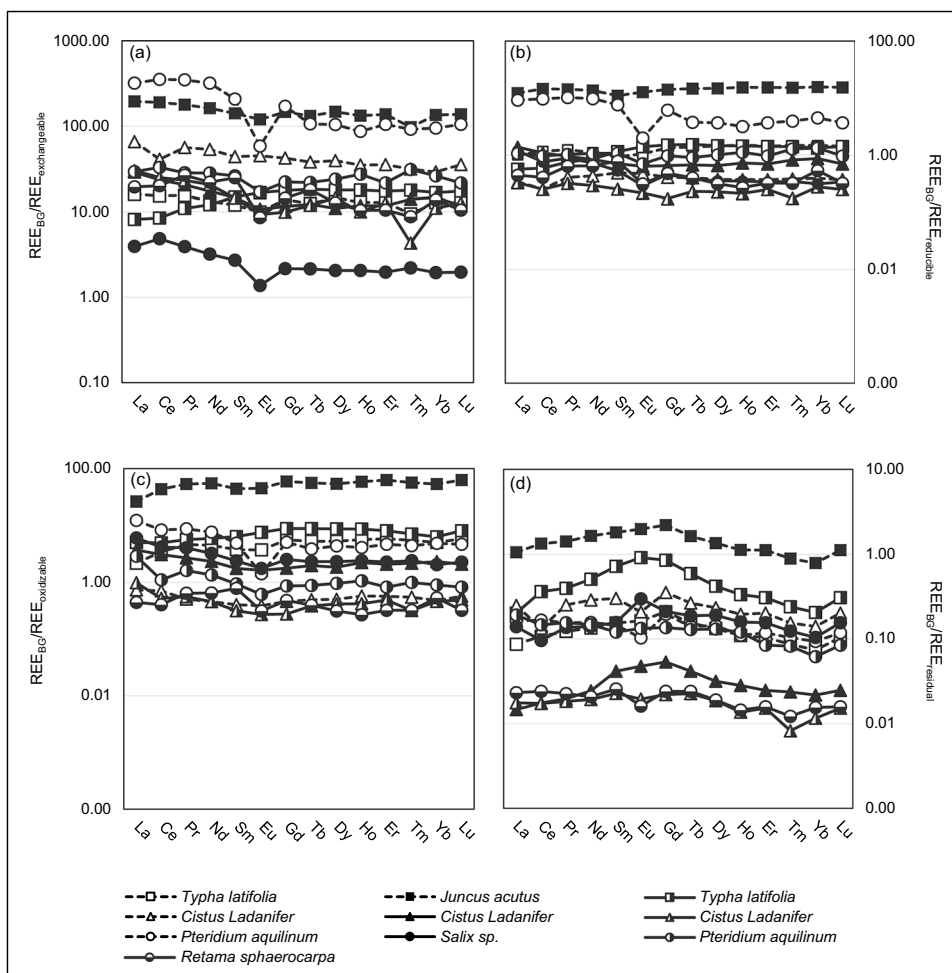


Fig. 4 Relative contents of REEs associated with the (a) exchangeable, (b) reducible, (c) oxidizable, and (d) residual soil fractions in belowground plant tissue. Samples from São

Domingos are indicated by triangles, samples from Quinta do Bispo are indicated by circles, and samples from Lousal are indicated by squares

have reported that in natural soils, the majority of soil REEs are bound to the residual fraction (Cao et al. 2022; Pang et al. 2002; Pédrot et al. 2009; Xinde et al. 2000; Zhang et al. 2023), with the exception of soils associated with certain mining waste streams (Khorasanipour and Rashidi 2020). Presumably, the lower proportions of REEs associated with the exchangeable, reducible, and oxidizable soil fractions in samples collected inside the mining site can be attributed to alteration of exchange surfaces and the dissolution of REE-bearing minerals due to the generation of AMD, leaving only recalcitrant or residual REE fractions. Compared with the samples taken from inside the mining sites, the samples collected from

the passive treatment system at Lousal had the highest proportion of non-recalcitrant REEs. The sediment collected from the Lousal treatment system was a composite of plant growth media, eroded material from the surroundings, and newly formed precipitates, which explains the differences in REE fractionation observed across these systems.

The sediment samples collected in this study exhibited distinct depletion of MREEs in the recalcitrant phase. This could be interpreted as evidence of the greater lability of MREEs over LREEs and HREEs in these systems. Both Grawunder et al. (2014) and Pérez-López et al. (2010) made similar observations but attributed the mobility of REE

to alteration of sulfide minerals, resulting in soluble MREE-sulfate complexes. In this study, both oxidizable and reducible fractions show MREE enrichment and could contribute to the observed MREE enrichment in AMD. This was in agreement with an article published by Khorasanipour and Rashidi (2020) who found the reducible minerals could play a significant role in controlling REE release from mining sites. Inside the treatment system at Lousal, REE fractionation shifted, and the relative content in the reducible fraction grew significantly. This change was accompanied by a larger proportion of LREEs associated with the reducible fraction. The relative proportions of LREEs and MREEs were comparable in the reducible (33% LREEs, 30% MREEs) and residual (61% LREEs, 62% MREEs) fractions. Similarly, a study of another passive treatment system installed by EDM in Jales, Portugal, revealed an association between REEs and Fe-oxide ochre precipitates formed in the limestone treatment basins (Prudêncio et al. 2015). It was concluded that the ochre precipitates scavenged more LREEs, causing an increase in the observed LREE/MREE ratio. These ochre precipitates were vulnerable to changes in hydrology and chemistry, leading to seasonal similarities in LREE/MREE ratios between effluents and precipitates (Prudêncio et al. 2015). Obregón-Castro et al. (2023) investigated similar samples from Lousal and found that most of the materials were Fe-oxyhydroxides with a large proportion of jarosite. Medium REEs with slight enrichment of LREEs over HREEs have been recorded in jarosite minerals (Obregón-Castro et al. 2023; Welch et al. 2009). Therefore, in this study, we attribute the increased percentage of REEs associated with the exchangeable fraction to the formation of jarosite in sample L-02, which is supported by the characteristic increases in the LREE/MREE ratios reported by Obregón-Castro et al. (2023) and Welch et al. (2009).

The Ce/Ce^* and Eu/Eu^* results revealed common themes across the REE patterns for the mining sites. The oxidizable fraction of the mining soils and sediments in this study is dominated by volcanogenic sulfide minerals and lower contents in organic matter. Similar positive Ce/Ce^* values have been observed in sulfides, which may originate in oceanic waters and sediments enriched in Ce (Otake et al. 2021). The geology could therefore account for the positive Ce/Ce^* in the oxidizable fraction. The negative Ce/Ce^* in the oxidizable fraction for the soil collected from

outside São Domingos was also reported for soils and surface waters in this area by Forsyth et al. (2023). The negative Ce/Ce^* in the oxidizable fraction may indicate preferential oxidation of Ce and subsequent Ce depletion in the reduced minerals. The negative Ce/Ce^* could also result from the formation of stable Ce complexes with microbially mediated organic acids, which has been shown to produce a negative Ce/Ce^* for mineral surfaces and increase Ce mobility (Kraemer et al. 2017).

For the soils collected inside the mining-impacted areas, the highly oxidizing nature of AMD waste may promote Ce oxidation, leading to the depletion of Ce in the oxidizable fraction and enrichment of Ce in surface complexes (exchangeable) and in the matrix of secondary minerals such as Fe-oxides (reducible). In this study, some samples had a slightly positive Ce/Ce^* in the reducible fraction. One such sample was collected from the treatment system at Lousal, and there are multiple possible explanations for the observed Ce/Ce^* value. As the passive treatment system is based on a wetland system, soil organic matter (SOM) may be responsible for trapping Ce. However, Pédrot et al. (2015) examined the combined effects of SOM and Fe-oxides on the behavior of REEs and found that Ce/Ce^* was mainly controlled by the Fe-oxide phase. Congruent with Pédrot et al. (2015), secondary mineral precipitates in the Lousal treatment system could scavenge any oxidized Ce, thereby producing a positive Ce/Ce^* in the reducible fraction.

The geochemical conditions in which soil phases were formed and weathered are important background information when making comparisons across studies and sites. As indicated in the [materials and methods](#) section, the soils collected from inside and outside the mining area differ in origin and pedogenesis. These differences are highlighted by the BCR extraction results. Although these soils are not directly comparable, the results provide valuable insight into the REE patterns established inside and outside the mining areas.

Bioavailability fingerprinting

As exemplified by a study of Vermeire et al. (2016), abiotic and biotic weathering of soils, sediments, and host rocks can change the fractionation and the amounts of bioavailable REEs in topsoil horizons. The following section explains the observed

partitioning of REEs in the context of biological weathering processes and defines a bioavailable pool.

The increase in the exchangeable REE pool in rhizosphere soils vs. bulk soils may be caused by carboxylic acids affecting the solubility of REEs in the rhizosphere, as theorized by Wiche and Pourret (2023). This mechanism may also explain some of the patterns observed in the soil-normalized REE_{BG} data. Typically, a MREE enrichment is associated with the monodentate complexation, while a HREE preference has been reported for stronger binding sites. Although simple carboxylic acid groups tend to form weaker monodentate complexes in high REE saturated environments, the function of stronger binding sites, associated with multidentate complexation or other anionic functional groups, is more pronounced at lower REE concentrations (Marsac et al. 2010). Europium also has a particular affinity for carboxylic and phosphate functional groups, limiting the solubility of Eu in plant tissue by sorption onto microbial biomass or other surfaces in the rhizosphere (Texier et al. 2000; Tyler 2004). Interestingly, the plants collected from Quinta do Bispo had large negative Eu/Eu^* when

REE_{BG} was normalized to the REE liberated through sequential extraction. This would mean that in relation to the other REE, the amount of Eu liberated by sequential extraction is lower than what would be expected based on the REE patterns in plants. Since this was isolated to the Quinta do Bispo samples it may indicate an interaction between the specific geological setting of Quinta do Bispo and the physiology of the plants collected there. In particular, the Quinta do Bispo site is dominated by granitic material instead of sulphide minerals and the soil pH was generally higher at the Quinta do Bispo site (ranging from pH 5.4–6.0) than in the other two sites (ranging from 3.3 to 5.8). Both of these factors distinguish Quinta do Bispo and may explain the differences observed in Eu uptake.

In the context of AMD, geochemical observations suggest that (1) a substantial portion of the exchangeable REE fractions are mobilized by changes in surface charge caused by lower pH, (2) reducible REEs can be released through acid-driven dissolution of reducible minerals, and (3) oxidation processes during AMD evolution can lead to oxidizable REE

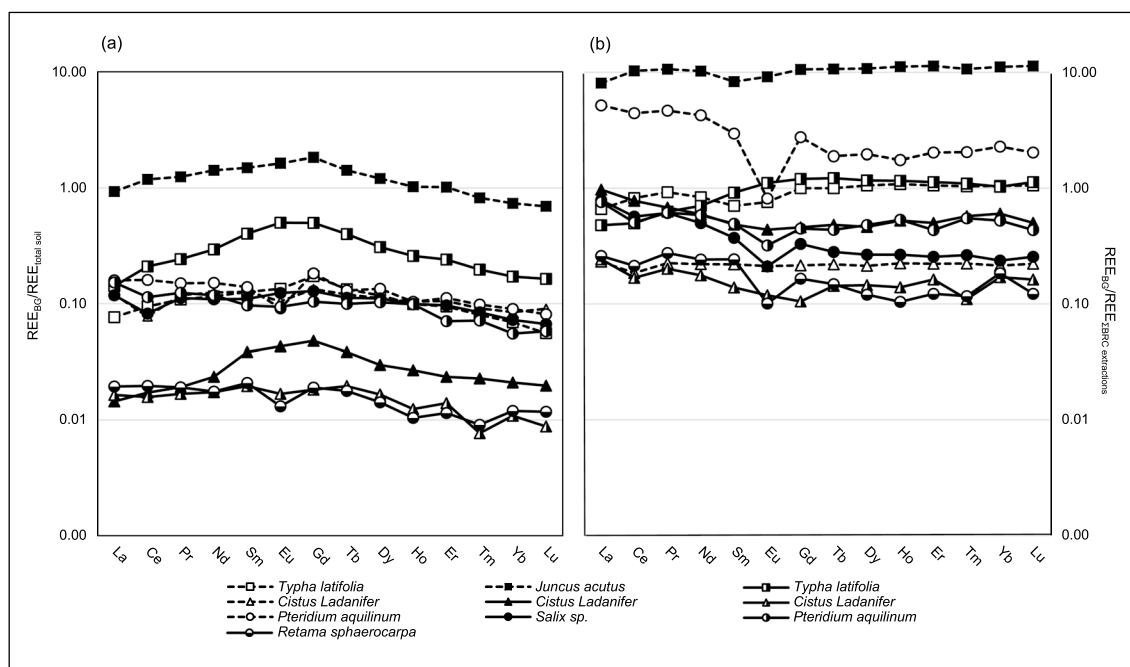


Fig. 5 (a) Data taken from Forsyth et al. (2023). The below-ground tissue contents are normalized to the total soil/sediment REE contents; (b) belowground tissue contents normalized to the sum of the contents of the three soil fractions identified by

sequential extraction. Samples from São Domingos are indicated by triangles, samples from Quinta do Bispo are indicated by circles, and samples from Lousal are indicated by squares

solubilization. Based on these assumptions, a labile pool of REEs could be operationally defined. Figure 5a and b compare the REE_{BG} concentrations normalized to the total soil REE contents (Fig. 5a) with the REE_{BG} concentrations normalized to the operationally defined labile REEs (Fig. 5b). Normalization of the belowground tissue data to the BCR extraction data changed the scale of the observations, with the values for all but one of the plant samples falling within one order of magnitude of 1.00. Moreover, the trend in the BCR extraction-normalized REE_{BG} data exhibited little to no slope or concavity (Fig. 5b), in contrast to the total soil REE-normalized REE_{BG} data (Fig. 5a), except for samples collected from Quinta do Bispo, which had a negative Eu/Eu^* and slight depletion in HREEs. These trends can be taken as qualitative evidence that the BCR extraction results reflect REE uptake by the investigated plants fairly well.

Conclusions

Soil is a complex medium, and it is difficult to predict the bioavailability of an element based on chemical extractions alone. Some studies have tried to address this topic by comparing different chemical extraction methods and determining which extracts best correlate with plant uptake of REEs. While sequential selective extractions provide valuable information on the behavior of elements, particularly their mobility, they do not accurately reflect their phytoavailability. This study related REE patterns for soil and sediment fractions to belowground plant tissue to determine the potential sources of REE in spontaneous vegetation around mining sites. These mining sites are characterized by the dissolution of oxidizable and reducible fractions. Rare earth elements in the soil were mainly associated with the residual fraction, which was depleted in MREEs. Accordingly, MREE enrichment was observed in the “exchangeable and carbonate-bound”, “reducible mineral”, and “oxidizable mineral and organic” fractions, which were more vulnerable to desorption and dissolution promoted by the geochemical conditions accrued from mining activity. As a result, the fractions from all three sequential extraction steps were operationally defined as the plant-available fraction in this system.

The concentrations of REEs in belowground plant tissue were in good agreement with the sum

of the REEs associated with the three sequential extraction steps. This was demonstrated by the normalization of the belowground tissue contents to the operationally defined available REEs, which showed that the shape and scale of the REE patterns were smoother than the soil-normalized data and distributed around 1.00. However, the Eu data deviated from this trend, as there was a distinct negative Eu/Eu^* for the Quinta do Bispo samples. There was a negative Eu/Eu^* in the tissue coupled with a positive Eu/Eu^* for the defined labile pools, indicating the exclusion of Eu from plant tissue despite the abundance of Eu in less recalcitrant soil fractions.

Although the insight provided here is valuable for determining the controlling factors of REE uptake in plant roots in mining environments, further studies should consider a variety of geological contexts and pH conditions. Additionally, further studies should be planned to determine the biological factors controlling or limiting plant uptake of REEs. To focus on phytoextraction, a more thorough assessment of the element’s physical and chemical speciation is required. Such studies could include the investigation of plant nutrient acquisition and how it relates to the plant availability of REEs.

Acknowledgements The authors are grateful for support from the GeOHeLiS analytical platform of Rennes. This publication is also supported by the European Union through the European Regional Development Fund (FEDER), the French Ministry of Higher Education and Research, and the French Region of Brittany and Rennes Métropole.

Author contributions **Kaisa Forsyth:** Writing – Original Draft, Investigation, Data Curation; **Aline Dia:** Conceptualization, Supervision, Writing – Review & Editing, Funding acquisition; **Rosa Marques:** Conceptualization, Writing – Review & Editing, Resources; **Maria Isabel Prudêncio:** Conceptualization, Writing – Review & Editing; **Cynthia Obregón-Castro:** Writing – Review & Editing, Data Curation; **Catarina Diamantino:** Writing – Review & Editing, Resources; **Edgar Carvalho:** Writing – Review & Editing, Resources; **Maxime Pattier:** Formal analysis; **Mélanie Davranche:** Conceptualization, Funding acquisition; **Mathieu Pédro:** Conceptualization, Supervision, Writing – Review & Editing.

Funding This project received funding from the European Union’s Horizon 2020 Research and Innovation Program under the Marie Skłodowska-Curie Grant Agreement No. 857989 (PANORAMA project).

Data availability The datasets generated and/or analyzed during the current study are available from the corresponding author upon request.

Declarations

Competing interests The authors have no relevant financial or nonfinancial interests to disclose.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

References

- Álvarez-Valero AM, Pérez-López R, Matos J, Capitán MA, Nieto JM, Sáez R, Delgado J, Caraballo M (2008) Potential environmental impact at São Domingos mining district (Iberian Pyrite Belt, SW Iberian Peninsula): evidence from a chemical and mineralogical characterization. *Environ Geol* 55:1797–1809
- Aries S, Valladon M, Polvé M, Dupré B (2000) A routine method for oxide and hydroxide interference corrections in ICP-MS chemical analysis of environmental and geological samples. *Geostandard Newsl* 24(1):19–31. <https://doi.org/10.1111/j.1751-908X.2000.tb00583.x>
- Baker JP, Bernard DP, Christensen SW, Sale MJ, Freda J, Heltcher K, Rowe L, Scanion P, Stokes P, Suter G, Warren-Hicks W (1990) Biological effects of changes in surface water acid-base chemistry. Department of Energy, (United States). <https://doi.org/10.2172/7255574>
- Barbosa SVT (2012) Modelação de atributos hidrogeológicos do maciço envolvente à antiga área mineira da Quinta do Bispo. Ph.D. Thesis, Universidade Nova de Lisboa, Lisboa, Portugal. <http://hdl.handle.net/10362/9059>
- Brioschi L, Steinmann M, Lucot E, Pierret MC, Stille P, Prunier J, Badot PM (2013) Transfer of rare earth elements (REE) from natural soil to plant systems: implications for the environmental availability of anthropogenic REE. *Plant Soil* 366:143–163
- Cao Y, Liu X, Wang C, Bai E, Wu N (2022) Rare earth element geochemistry in solid along arid and semiarid grasslands in Northern China. *Ecol Process* 11:29
- Cardenas A, Dias MI, Diamantino C, Carvalho E, Russo D (2023) Geochemical behavior of lanthanides and actinides in an old uranium mine, Portugal. *Geosci J* 13:168
- Davranche M, Pourret O, Gruau G, Dia A (2004) Impact of humate complexation on the adsorption of REE onto Fe oxyhydroxide. *J Colloid Interface Sci* 277:271–279
- Dia A, Gruau G, Olivé-Lauquet G, Riou C, Molénat J, Curmit P (2000) The distribution of rare earth elements in groundwaters: assessing the role of source-rock composition, redox changes and colloidal particles. *Geochim Cosmochim Acta* 64(24):4131–4151
- Durães N, Bobos I, Ferreira da Silva E (2017) Speciation and precipitation of heavy metals in high-metal and high-acid mine waters from the Iberian Pyrite Belt (Portugal). *Environ Sci Pollut Res* 24:4562–4576
- Empresa de Desenvolvimento Mineiro and Direção-Geral de Energia e Geologia (2011) The legacy of Abandoned Mines: the Context and the action in Portugal. Lisboa, Portugal
- Ferreira RA, Pereira MF, Magalhães JP, Maurício AM, Caçador I, Martin-Dias S (2021) Assessing local acid mine drainage impacts on natural regeneration-vegetation of São Domingos mine (Portugal) using a mineralogical, biochemical, and textural approach. *Sci Total Environ* 755(1):1–16
- Ferreira da Silva E, Bobos I, Xavier Matos J, Patinha C, Reis AP, Fonseca C (2009) Mineralogy and geochemistry of trace metals and REE in volcanic massive sulfide host rocks, stream sediments, stream waters and acid mine drainage from the Lousal mine area (Iberian Pyrite Belt, Portugal). *Appl Geochem* 24(3):383–401
- Forsyth K, Dia A, Marques R, Prudêncio MI, Diamantino C, Carvalho E, Russo D, Dionisio I, Davranche M, Bouhnik-Le-Coz M, Pédrot M (2023) Bioconcentration and translocation of rare earth elements in plants collected from three legacy mine sites in Portugal. *Front Environ Sci* 11:1191909. <https://doi.org/10.3389/fenvs.2023.1191909>
- Gong B, He E, Romero-Freire A, Ruan J, Yang W, Zhang P, Qiu H (2021) Do essential elements (Pa and Fe) have mitigation roles in the toxicity of individual and binary mixture of yttrium and cerium in *Triticum aestivum*? *J Hazard Mater* 416:125761
- Gonzalez V, Vignati DAL, Leyval C, Giamberini L (2014) Environmental fate and toxicity of lanthanides: are they a uniform group beyond chemistry? *Environ Int* 7:148–157
- Grawunder A, Merten D, Büchel G (2014) Origin of middle rare earth element enrichment in acid mine drainage-impacted areas. *Environ Sci Pollut Res* 21:6812–6823
- Khorasanipour M, Rashidi S (2020) Geochemical fractionation pattern and environmental behaviour of rare earth elements (REEs) in mine wastes and mining contaminated sediments; Sarcheshmeh mine, SE of Iran. *J Geochem Explor* 210:106450
- Kong Z, Glick BR (2017) The role of plant-growth promoting bacteria in metal phytoremediation. *Adv Microb Physiol* 71:97–132
- Kraemer D, Tepe N, Pourret O, Bau M (2017) Negative cerium anomalies in manganese (hydr)oxide precipitates due to cerium oxidation in the presence of dissolved siderophores. *Geochim Cosmochim Acta* 196:197–208
- Kubová J, Matuš P, Bujdoš M, Hagarová I, Medved J (2008) Utilization of optimized BCR three-step sequential and dilute HCl single extraction procedures for soil-plant

- metal transfer predictions in contaminated lands. *Talanta* 75:1110–1122
- Li X, Chen Z, Chen Z, Zhang Y (2013) A human risk assessment of rare earth elements in soil and vegetables from a mining area in Fujian Province, Southeast China. *Chemosphere* 93:1240–1246
- Liang T, Zhang S, Wang L, Kung HT, Wang Y, Hu A, Ding S (2005) Environmental biogeochemical behaviors of rare earth elements in soil-plant systems. *Environ Geochem Health* 27:301–311
- Liang T, Ding S, Song W, Chong Z, Zhang C, Li H (2008) A review of fractionations of rare earth elements in plants. *J Rare Earth* 26:7–15
- Luís AT, Teixeira P, Almeida SFP, Matos JX, Ferreira da Silva E (2011) Environmental impact of mining activities in the Lousal area (Portugal): Chemical and diatom characterization of metal-contaminated stream sediments and surface water of the Corona stream. *Sci Total Environ* 409(20):4312–4325
- Marsac R, Davranche M, Gruau G, Dia A (2010) Metal loading effect on rare earth element binding to humic acid: experimental and modelling evidence. *Geochim Cosmochim Acta* 74(6):1749–1761. <https://doi.org/10.1016/j.gca.2009.12.006>
- Matos JX, Pereira Z, Rosa CJP, Oliveira JT (2014) High resolution stratigraphy of the Phyllite-Quartzite Group in the northwestern region of the Iberian Pyrite Belt, Portugal. *Comunicações Geológicas* 101(Especial I):489–493
- Matos-Dias JM, Costa CVB (1972) A região uranífera Da Cunha Baixa-Quinta do Bispo. *Memórias E Notícias. Publicações do Museu e Laboratório de Mineralogia. Universidade de Coimbra*, pp 24
- Merschel G, Bau M (1995) Rare earth elements in the aragonitic shell of freshwater mussel *Corbicula fluminea* and the bioavailability of anthropogenic lanthanum, samarium and gadolinium in river water. *Sci Total Environ* 533:91–101
- Migaszewski ZH, Gałuszka A (2015) The characteristics, occurrence, and geochemical behavior of rare earth elements in the environment: a review. *Environ Sci Technol* 45:429–471
- Morais I, Albardeiro L, Batista MJ, Matos JX, Solá R, de Oliveira DPS, Salgueiro R, Araújo V, Pacheco N (2020) Geochemistry of Iberian Pyrite Belt Portuguese sector massive sulphide deposits-related volcanic rocks. Considerations on hydrothermal alteration, petrology and tectonic evolution. *Comunicações Geológicas* 107(III):133–149
- Obregón-Castro C, Prudêncio MI, Waerenborgh JC, Vieira BJC, Diamantino C, Carvalho E, Marques R (2023) July 9–14) Distribution and fractionation of rare earth elements in a passive treatment system installed in a legacy polymetallic sulfide mine. [Poster]. *Goldschmidt 2023*, Lyon, France. <https://conf.goldschmidt.info/goldschmidt/2023/meetingapp.cgi/Paper/19148>. Accessed 21 Sept 2023
- Oliveira VJM, Matos JX, Rosa C (2001) The NNW sector of the Iberian Pyrite Belt – new exploration perspectives for the next decade. *Geode Workshop – Massive sulphide deposits in the Iberian Pyrite Belt: new advances and comparison with equivalent systems, Aracena Spain*, pp 34–37
- Otake T, Yamada R, Suzuki R, Nakamura S, Ito A, Shin K, Sato T (2021) Large Fe isotope fractionations in sulfide ores and ferruginous sedimentary rocks from Kuroko volcanogenic massive sulfide deposits in the Hokuroku district, northeast Japan. *Geochim Cosmochim Acta* 295:49–64
- Pagano G, Aliberti F, Guida M, Oral R, Siciliano A, Trifuoggi M, Tommasi F (2015) Rare earth elements in human and animal health: state of the art and research priorities. *Environ Res* 142:215–220
- Pang X, Li D, Peng A (2002) Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. *Environ Sci Pollut R* 9:143–148
- Pédrot M, Dia A, Davranche M, Gruau G (2009) Double pH control on humic substance-borne trace elements distribution in soil waters as inferred from ultrafiltration. *J Colloid Interface Sci* 339(2):390–403
- Pédrot M, Dia A, Davranche M, Gruau G (2015) Upper soil horizons control the rare earth element patterns in shallow groundwater. *Geoderma* 239–240:84–96
- Pereira Z, Matos J, Fernandez P, Oliveira JT (2008) Palynostratigraphy and systematic palynology of the devonian and carboniferous successions of South Portuguese Zone, Portugal. *Memórias. do Instituto Nacional de Engenharia, Tecnologia, e Inovação (Lisboa, Portugal: INETI)*
- Pereira R, Barbosa S, Carvalho FP (2014) Uranium mining in Portugal: a review of the environmental legacies of the largest mines and environmental and human health impacts. *Environ Geochem Health* 36:285–301
- Pérez-López R, Álvarez-Valero AM, Nieto JM, Sáez R, Matos JX (2008) Use of sequential extraction procedure for assessing the environmental impact at regional scale of the São Domingos Mine (Iberian Pyrite Belt). *Appl Geochem* 23(12):3452–3463
- Pérez-López R, Delgado J, Nieto JM, Márquez-García B (2010) Rare earth element geochemistry of sulphide weathering in the São Domingos mine area (Iberian Pyrite Belt): proxy for fluid-rock interaction and ancient mining pollution. *Chem Geol* 276(1–2):29–40
- Pourret O, Davranche M, Gruau G, Dia A (2007) Rare earth elements complexation with humic acid. *Chem Geol* 243:128–141
- Prudêncio MI, Valente T, Marques R, Braga S, Pamplona MA (2015) Geochemistry of rare earth elements in a passive treatment system built for acid mine drainage remediation. *Chemosphere* 138:691–700
- Quental L, Bourguignon A, Sousa AJ, Batista MJ, Brito MG, Tavares T, Abreu MM, Vairinho M, Cottard F (2002) MINEO Southern Europe environment test site: Contamination impact mapping and modelling — Final Report [Report No. IST-1999-10337]. Information Society Technologies. <http://hdl.handle.net/10400.9/3268>
- Ramalho E, Carvalho J, Barbosa S, Monteiro Santos FA (2009) Using geophysical methods to characterize an abandoned uranium mining site, Portugal. *J Appl Geophys* 67:14–33
- Rim KT, Koo KH, Park JS (2013) Toxicological evaluations of rare earths and their health impacts to workers: a Literature Review. *Saf Health Work* 4(1):12–26
- Sessitsch A, Kuffner M, Kidd P, Vangronsveld J, Wenzel WW, Fallman K, Puschenreiter M (2013) The role of plant-associated bacteria in the mobilization and phytoextraction of

- trace elements in contaminated soils. *Soil Biol Biochem* 60:182–194
- Shan X, Wang Z, Wang W, Zhang S, Wen B (2003) Labile rhizosphere soil solution fraction for prediction of bioavailability of heavy metals and rare earth elements. *Anal Bioanal Chem* 375:400–407
- Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr A* 32:751–767
- Soyol-Erdene TO, Valente T, Grande JA, de la Torre ML (2018) Mineralogical controls on mobility of rare earth elements in acid mine drainage environments. *Chemosphere* 205:317–327
- Stille P, Steinmann M, Pierret MC, Gauthier-Lafaye F, Aubert D, Probst A, Viville D, Chabaux F (2006) The impact of vegetation on fractionation of rare earth elements (REE) during water-rock interaction. *J Geochem Explor* 88(1–3):341–344
- Tang J, Johannesson KH (2003) Speciation of rare earth elements in natural terrestrial waters: assessing the role of dissolved organic matter from the modeling approach. *Geochim Cosmochim Acta* 67(13):2321–2339
- Taylor SR, McLennan SM (1985) *The continental crust: its composition and evolution*. Blackwell, Oxford
- Texier AC, Andrès Y, Illemassene M, Le Cloirec P (2000) Characterization of lanthanide ions binding sites in the cell wall of *Pseudomonas aeruginosa*. *Environ Sci Technol* 34:610–615
- Tyler C (2004) Rare earth elements in soil and plant systems - a review. *Plant Soil* 267:191–206
- Ure AM, Quevauviller P, Muntau H, Griepink B (1993) Speciation of heavy metal in soils and sediments. An account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the commission of the European communities. *Int J Environ Anal Chem* 51:135–151
- Van Gosen BS, Verplanck PL, Seal RR, Long KR II, Gambogi J (2017) Chapter O: Rare-earth elements. In: Schulz KJ, DeYoung JH Jr, Seal RR II, Bradley DC (eds) *Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply*, (Reston, VA: U.S. Geological Survey), O1–O31. <https://doi.org/10.3133/pp18020>
- Vermiere ML, Cornu S, Fekiacova Z, Detienne M, Delvaux B, Cornélis JT (2016) Rare earth elements dynamics along pedogenesis in a chronosequence of podzolic soils. *Chem Geol* 446:163–174
- Wakabayashi T, Ymamoto A, Kazaana A, Nakano Y, Nojiri Y, Kashiwazaki M (2016) Antibacterial, antifungal and nematocidal activities of rare earth ions. *Biol Trace Elem Res* 174(2):464–470
- Wang Q, Huang B, Guan Z, Yang L, Li B (2001a) Speciation of rare earth elements in soil by sequential extraction then HPLC coupled with visible and ICP-MS detection. *Fresenius J Anal Chem* 370:1041–1047
- Wang Z, Shan X, Zhang S (2001b) Comparison of speciation and bioavailability of rare earth elements between wet rhizosphere soil and air-dried bulk soil. *Anal Chim Acta* 441:147–156
- Welch SA, Christy AG, Isaacson L, Kirste D (2009) Mineralogical control of rare earth elements in acid sulfate soils. *Geochim Cosmochim Acta* 73:44–64
- Wiche O, Pourret O (2023) The role of root carboxylate release on rare earth element (hyper)accumulation in plants – a biogeochemical perspective on rhizosphere chemistry. *Plant Soil*. <https://doi.org/10.1007/s11104-023-06177-2>
- Wytenbach A, Tobler L, Schleppei P, Furrer V (1998a) Variation of the rare earth element concentrations in the soil, soil extract and in individual plants from the same site. *J Radioanal Nucl Ch* 231(1–2):101–106
- Wytenbach A, Furrer V, Schleppei P, Tobler L (1998b) Rare earth elements in soil and in soil-grown plants. *Plant Soil* 199:267–273
- Xinde C, Xiaorong W, Guiwen Z (2000) Assessment of the bioavailability of rare earth elements in soils by chemical fractionation and multiple regression analysis. *Chemosphere* 40:23–28
- Yéglicheyan D, Aubert D, Bouhnik-Le Coz M, Chmeleff J, Delpoux S, Djouaev I, Granier G, Lacan F, Piro J, Rousseau T, Cloquet C, Marquet A, Menniti C, Pradoux C, Freydier R, Vieira, da Silva-Filho E, Suchorski K (2019) A new interlaboratory characterisation of silicon, rare earth elements and twenty-two other trace element concentrations in the natural river water certified reference material SLRS-6 (NRC-CNRC). *Geostand Geoanal Res* 43(3):475–496
- Zhang S, Shan XQ (2001) Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application. *Environ Pollut* 112:395–405
- Zhang X, Du W, Xu Z, Cundy AB, Croudace IW, Zhang W, Jin H, Chen J (2023) The distribution and enrichment of trace elements in surface and core sediments from the Changjiang River Estuary, China: evidence for anthropogenic inputs and enhanced availability of rare earth elements (REE). *Mar Pollut Bull* 193:115082. <https://doi.org/10.1016/j.marpolbul.2023.115082>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.