scientific reports

OPEN

Redistribution and enhanced bioavailability of rare earth elements speciation induced by mining-driven transformation in ionic rare earth mining areas

Zengxue Wu[1], Jingjing Liu[1,2]✉, Chun Li[1], Wei Liu[3] & Weixiang Wu[4]

Mining is an anthropogenic activity, that alters rare earth elements (REEs) distribution, changes the ecological environment of mining areas, and pollutes surrounding areas. However, the impacts of mining activities on REEs distribution and chemical morphological changes in mining soils are still poorly understood. In the present study, REEs fractionation and chemical speciation in both mining and unexploited soils were investigated through BCR sequential extraction. Most of the soil samples presented positive cerium (Ce) anomalies and negative europium (Eu) anomalies. The ratios of light rare earth elements (LREEs) to heavy rare earth elements (HREEs) and the total rare earth elements (TREEs) contents in mining soil were lower than those in unexploited soil. In unexploited soils, REEs were dominated by the residual fraction, and the exchangeable fraction was the lowest, accounting for 50.85–91.41% and 0.15–13.02% of TREEs, respectively. Mining activities modified REEs chemical speciations, which notably increased the exchangeable fraction (0.47-56.00%) and decreased the residual fraction (4.62–65.01%) in mining areas. Moreover, the reducible fraction also significantly increased in mining soils, accounting for 21.15–63.29% of TREEs. Compared with the unexploited areas, the relationships between soil properties and REEs distribution in mining areas were more pronounced. However, mining activities exerted little effect on the chemical speciation of Fe and Al, and the proportions of the residual fraction were dominant both before and after mining. These results demonstrated that mining activities decreased the contents of TREEs, redistributed REEs chemical morphological patterns, and increased their mobility and bioavailability, which are the principal anthropogenic sources of REEs entering environments and increase the risk of soil pollution.

Keywords Mining activities, Rare earth elements, Fractionation, Chemical speciation, Bioavailability

Rare earth elements (REEs) are composed of lanthanides (La-Lu), scandium, and yttrium, with a total of 17 metallic elements. According to Oddo-Harkinsthe, even atomic-numbered elements have an order of magnitude greater abundance (higher Clarke concentrations) than their adjacent odd-numbered counterparts, and further emphasized by a greater number of isotopes. On the basis these properties, REEs are classified as light rare earths (LREEs, La-Lu) and heavy rare earths (HREEs, Gd and Tb-Lu)[1–3]. Because of its physical and chemical similarities, yttrium (Y) is typically classified as HREEs, although it is the lightest REE. REEs are essential strategic resources worldwide due to their unique physicochemical properties. They are extensively used in both high-tech and traditional industries, including the national defense and military, petroleum refining, permanent magnets, textiles, and others. REEs have made important contributions to the development of the national economy[4,5].

Ion-adsorption type REEs (ionic REEs), the most important REEs sources in the world, are uniquely formed from weathered granite crusts containing REEs minerals in warm and humid climates[6]. The primary reservoirs

[1]School of Energy and Machinery Engineering, Jiangxi University of Science and Technology, Shuanggang East Road #1180, Nanchang 330013, China. [2]Jiangxi Key Laboratory of Mining & Metallurgy Environmental Pollution Control, Ganzhou 341099, China. [3]College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China. [4]Institute of Environmental Science and Technology, Zhejiang University, Hangzhou 310030, China. ✉email: jingjingliu1985@163.com

of global ionic REEs are located in China, particularly in southern Jiangxi Province. This region possesses substantial ionic rare earth deposits[7]especially those rich in terbium, dysprosium, europium, yttrium, and other high-value medium and heavy REEs[8]. Ionic REEs can be extracted through a leaching technique with electrolyte solutions though an ion-exchange process due to their specific form[9]. In-situ leaching is the most effective technology to extract REEs, with a high leaching efficiency of up to 85–90%. It has become the standard mining technology for ionic REEs ores[10]. The most commonly used leaching solution is 3–5% ammonium sulfate ($(NH_4)_2SO_4$), with the leaching process spanning 150–400 days. In recent years, the development of the high-tech REEs industry and the global use of REEs-related products have promoted large-scale exploitation of rare earth resources, and also increased the possibility of REEs input into the environment[11]. Furthermore, REEs exploitation and mining activities not only result in the degradation of the original ecosystem, severe soil erosion, and biodiversity loss, but also contribute to the spread of REEs to surrounding areas[12]. Rainfall accompanied by natural leaching exacerbates damage to soil structures and nutrient loss. REEs exploitation has been one of the principal factors in soil degradation in southern China.

Previous studies have already emphasized the irreversible and severe adverse effects caused by mining activities on ecological environments[9]. Currently, research focuses on the increase of REEs contents in the surrounding soil and water, the impact of REEs mining on crops, and the transfer of REEs between soil and plants. The influence of REEs exploitation on soil properties and microorganisms in and around mining areas have been investigated as well[13,14]. The concentrations of REEs in soil and water near REEs mining areas have been proven to be significantly higher than the background values of soil REEs in Jiangxi Province and China, and REEs in main crops are far higher than the critical values harmful to human health[11]. Researchers reported that the potential anthropogenic sources in the soil around REEs mines are composed of mining-related leachate, traffic exhaust, and industrial dust[15]. Moreover, mining activities decreased the content of total rare earth elements (TREEs) and altered the vertical distributions of LREEs/HREEs and chemical speciations in weathering profiles[16]. The relevant researches were summarized in Table S1.

The total heavy metal concentration is a common and useful indicator of soil pollution in ecosystems. However, environmental problems driven by high heavy metal levels are more strongly related to their chemical speciations and bioavailability rather than to their total contents[17,18]. Previous studies have reported that mining activities not only translocated heavy metals into soils[19]but also significantly increased their potential bioavailability in mine tailings[20–22]. This exacerbates the threat to deep soil and the surrounding environment. Owing to the unique forms of ionic REEs, the REEs morphological changes caused by mining activities should directly affect the pollution characteristics in and around mining areas, as well as the corresponding environmental risks. However, little is known about the REEs distribution and speciation differences between unexploited and mining areas that might be influenced by mining activities. Hence, more attention should be given to the transformation of REEs fractions driven by anthropogenic exploitation, as relevant research is critical for assessing the ecological risks of REEs exploitation and developing targeted environmental management strategies.

Therefore, we investigated the morphology and geochemical characteristics of REEs in unexploited and mining areas in southern China. The main purposes of this study are to (1) clarify the differences in REEs distribution characteristics and chemical morphological patterns between mining soil and unexploited soil; (2) investigate the relative importance of REEs speciation and the physicochemical properties of soils on its bioavailability. This study could provide new insights into the environmental risks associated with ionic REEs exploitation.

Materials and methods

Study area and sampling collection

The study areas were located in Longnan and Dingnan Counties, southern Jiangxi Province, China. The four key factors, including REEs-rich granites, intense chemical weathering driven by high temperature and rainy climate, clay-rich weathering profiles with high adsorption capacity, and gentle topography allowing profile preservation, create the perfect conditions for forming ionic REEs deposits in this region. This area has a subtropical monsoonal humid climate with high precipitation and mild weather. The annual average precipitation is 1500–1600 mm and the mean temperature is 19.0 ℃. The study area is mountainous, which is famous for its abundant rare earth resources, with hills and mountains accounting for nearly 80% of the region. The dominant vegetation consists of coniferous pines and shrubs, and the soil is classified as red soil. Over the past several decades, in-situ leaching has been the primary method for REEs extraction. However, all mining activities have been restricted since 2016. In abandoned mining areas, most of the vegetations and topsoil have been removed to lay plastic pipes for transporting leaching solution. Additionally, many abandoned leaching holes remain visible across the mining areas, serving as clear indicators of prior mining operations. In September 2020, three sampling areas marked as LD, LE, and LN were arranged in abandoned mining areas without any soil remediation. The sampling sites were arranged via the systematic random distribution method and adjusted according to the actual geographical situation. Approximately 1000 g topsoil (0–15 cm) was collected at each sampling site, and each sample was a mixture of four subsamples randomly collected in a circle with a radius of 4 m, Forty mining soil samples (LD1-LD12, LE1-LE15, LN1-LN13) were randomly collected individually and placed in an independent sterile polyvinyl chloride bag. Another twelve samples, marked as LA1-LA12, were collected randomly using the same method in unexploited REEs mine areas, which were in another ore district and had not undergone any forms of extraction. A total of 52 topsoil samples were gathered by a stainless steel core soil sampler, and their geographic coordinates were recorded via a global position system, as illustrated in Supplementary Table S2 and Fig. S1.

Soil property analysis and REEs characteristic parameters analysis

Visible plant residues and roots were removed, and then each sample was divided into two parts. One part was preserved at 4 °C until the assessment of soil moisture content, organic matter, pH, ammonium, nitrite, and nitrate.Moisture content was represented by the difference of weight before and after drying at 105 °C for 24 h. Organic matter was analyzed by measuring the weight difference after combustion at 550 °C for 2 h. Soil pH and electrical conductivity (EC) were measured after shaking the soil water (1:2.5 w/v) suspension for 1 h, using a pH meter (Delta 320, Mettler Toledo, Switzerland) and an electrical conductivity meter (sensION^{TM}5, HACH, USA), respectively. Inorganic N (nitrate, nitrite and ammonium) was extracted with 2 M KCl (1:5 of soil: solution by mass) by shaking (1 h, 200 rpm) and filtering. The filtrate was sampled to determine by spectrophotometric method. The other portion was air-dried at ambient temperature and sieved through a 2 mm polyethylene mesh for REEs analyses. Some of the air-dried soil was ground into fine powder using an agate mortar and then passed through a 0.075 mm nylon sieve for total carbon (TC), total nitrogen (TN), and total sulhur (TS) analysis, using an Elemental analyzer (Vario MAX CNS, Elementar Analysesysteme, Germany).

TREEs are composed of elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. LREEs are the sum of La, Ce, Pr, Nd, Sm, and Eu. HREEs are the sum of the Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. BCR (Bureau Communautaire de Référence) sequential extraction was conducted to investigate the different chemical speciations of REEs in each soil sample: exchangeable fraction (F1), reducible fraction (F2) that bound Fe/Mn oxides, oxidizable fraction (F3) that bound to organic matter, and residual fraction (F4)[16]. The BCR procedure was described shown in the Supplementary Information (Fig. S2). The concentration of REEs in the extracted solutions of each step was ultimately measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 8800 Triple Quadrupole, Agilent Technologies, US). The limit of detection (LOD) was 0.01 μg/L, and the limit of quantitation (LOQ) was 0.03 μg/L. The major elements Fe and Al were also analyzed. A calibration curve was prepared from a standard solution for each element, and the linear standard curves were better than 0.999 for all elements. To determine the precisions of the BCR method, all the samples were extracted in triplicate, and the relative standard deviation (RSD) in the fraction of F1 to F3 was below 6% on average. The contents of F1, F2, F3, and F4 were calculated based on the sum of 15 exchangeable, reducible, oxidizable, and residual REEs fractions, respectively. Fractionation characteristics of LREEs and HREEs were evaluated using La_N/Sm_N, Gd_N/Yb_N, and La_N/Yb_N ratios to illustrate their geochemical patterns[23]. An anomaly of REEs indicated their enrichment or depletion relative to neighboring REEs, and Ce(Ce/Ce*) and Eu(Eu/Eu*) could be calculated using the following Eqs[24,25]..

$$\delta Ce = \frac{Ce}{Ce^{*}} = \frac{Ce_N}{(La_N \times Pr_N)^{0.5}} \delta Eu = \frac{Eu}{Eu^{*}} = \frac{Eu_N}{(Sm_N \times Gd_N)^{0.5}} (La/Sm)_N = La_N/Sm_N$$

$$(La/Yb)_N = La_N/Yb_N (Gd/Yb)_N = Gd_N/Yb_N$$

Statistical analysis

Statistical analyses were conducted by SPSS software (version 19.0) to explore the relationships between REEs and soil properties. An independent sample *t*-test (Student *t*-test or Welch's *t*-test) was applied to test the differences in the actual content and proportion of the four REEs fractions between unexploited soils and mining soils. To validate the assumption of homogeneity of variances for the *t*-test, we performed Levene's test. ArcMap 10.0 was used to generate a sampling distribution map. The mental test reflected the relative effects of environmental variables on REEs speciation in different soils, and displayed correlations using R software(version 4.1.2). Line graphs, Pearson correlations, and biplots were applied, and the figures above were drawn via Origin 2018.

Results

Characteristics of REEs chemical speciation patterns

Chemical speciation analysis of soils from 52 sampling points within mining areas and unexploited areas was carried out via the BCR sequential extraction method. The extracted morphological forms included exchangeable, reducible, oxidizable, and residual fractions (Fig. 1 and Fig. S3).

TREEs in unexploited soil (LA) range from 590 to 780 mg/kg. The mean percentage distributions of the REEs four fractions in unexploited soils showed similar trends as follows: exchangeable (F1) < reducible (F2) < oxidizable (F3) < residual (F4). F1 presented the lowest content from 1.11 to 85.95 mg/kg, accounting for 0.15–13.02% of TREEs. F4 exhibited the highest content and accounted for 50.85–91.41% of TREEs.

Remarkable discrepancies in REEs contents existed among the different sampling points in the mining areas. The TREEs content of mining soils (LD, LE, and LN) varied over a broad range from 100 to 790 mg/kg, with a median of 373.25 mg/kg. The average percentage of each fraction showed a consistent trend following the gradient F3 < F1 < F4 < F2. The proportion of exchangeable fraction (F1) represented 3.79%−48.71% of TREEs, which was significantly greater than that in unexploited soils (Fig. 2). While the proportion of residual fraction (F4) notably decreased and ranged from 32.82 to 209.76 mg/kg (4.62%−60.08%), and both the actual content and proportion were extremly and significantly lower than those of unexploited soil. The contents of reducible fraction (F2) in mining soils were significantly greater than that of unexploited soils, accounting for 21.15–69.33% of TREEs.

Distribution pattern of REEs fractionation

In mining soils, LREEs varied from 41.65 to 191.25 mg/kg, and HREEs ranged from 43.30 to 618.90 mg/kg. Unexploited soils contained higher contents of LREEs than HREEs, whereas the mining soil samples exhibited more HREEs than LREEs. Furthermore, both mining and unexploited soils complied with *the oddo-Harkins rule*, which illustrated that elements with even atomic numbers (Ce, Nd, Sm, Gd, Er, and Yb) were more abundant than those with adjacent odd atomic numbers (La, Pr, Eu, Tb, Ho, Tm and Lu) (Fig. 3). As the highest content of HREEs, Y accounted for 15.28% and 51.71% of TREEs in the mining soils and unexploited soils, respectively. Due to their high content, HREEs accounted for over 70% of TREEs in mining soil samples. Ce was the most abundant LREE, ranging from 15 mg/kg to 260 mg/kg. In unexploited soil, the proportion of Ce within TREEs was significantly higher than that in mining soil, which led to a greater proportion of LREEs in unexploited

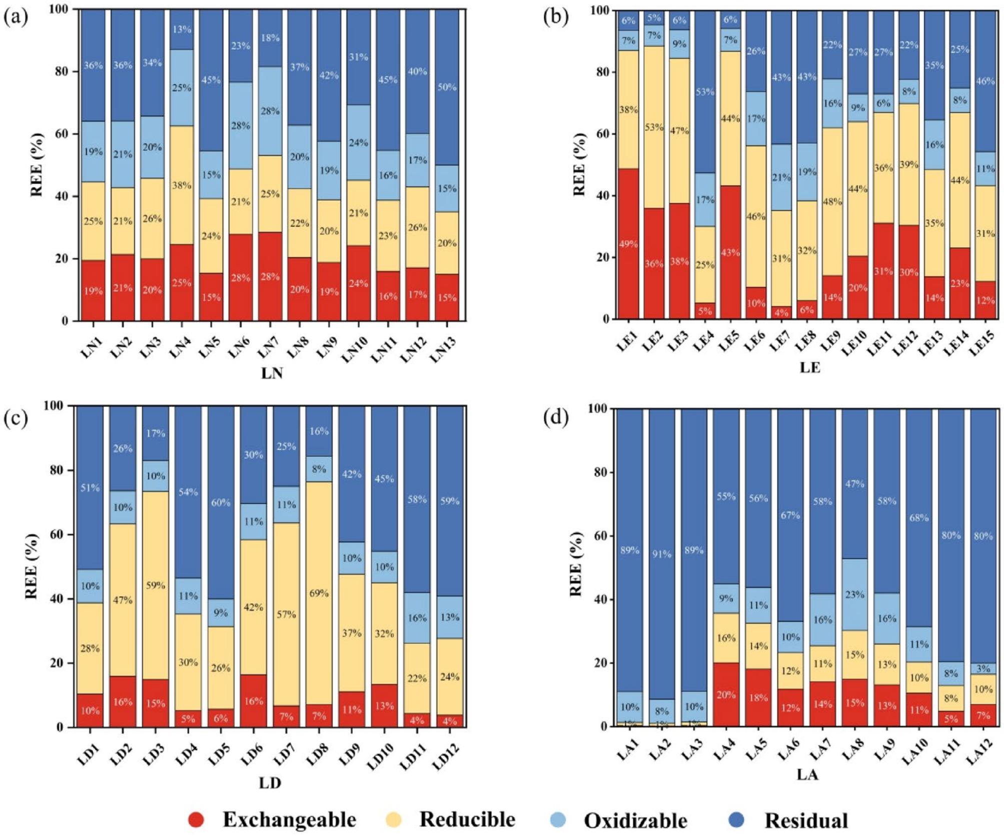

Fig. 1. The proportion of REEs fractions in all the soil samples.

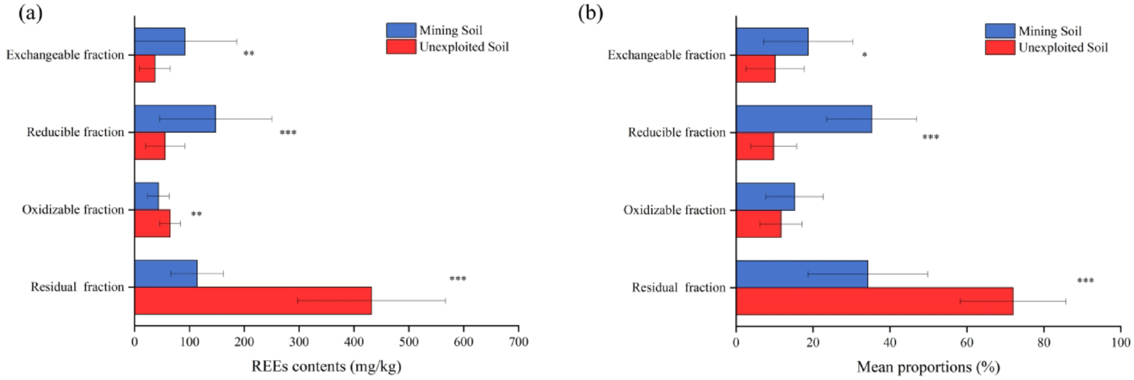

Fig. 2. The statistical comparisons of actual content (**a**) and proportion (**b**) of REEs fractions in unexploited soil and mining soil (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$).

soil (75.39%) than in mining soil (25.81%). These two elements represented more than 50% of TREEs in all the samples.

The normalized REEs distributions in mining soils were consistent, with the curves of LN, LD, and LE downwards from right to left. While the normalized curve of unexploited soil (LA) tilted from left to right, and exhibited steep in La-Eu and flat in Dy-Lu (Fig. 4). Bivariate plots of REEs fractionations revealed different fractionation characteristics of LREEs and HREEs in unexploited soils and mining soils (Fig. 5). The range of LREEs/HREEs variation within unexploited soil (LA) spanned from 2.25 to 4.16, with an arithmetic mean of 3.20, which were much higher than those of mining soils. These samples also exhibited a La_N/Yb_N spectrum spanning from 6.91 to 14.11, demonstrating a conspicuous divergence between light and heavy REEs. Conversely, the LREEs/HREEs values in most mining soil samples were less than one, falling within the interval of 0.15 to 1.63. The values of La_N/Yb_N notably deviated downwards from those of unexploited soil, indicating a comparatively less pronounced partitioning between LREEs and HREEs in the mining area. The LREEs fractionation assessed

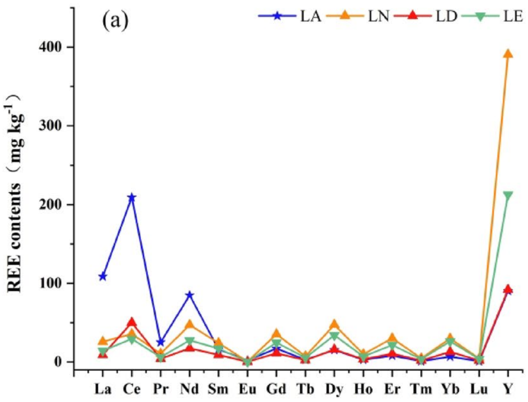

Fig. 3. The contents (**a**) and percentages (**b**) of REEs species in the four sampling sites (LA, LD, LN, LE).

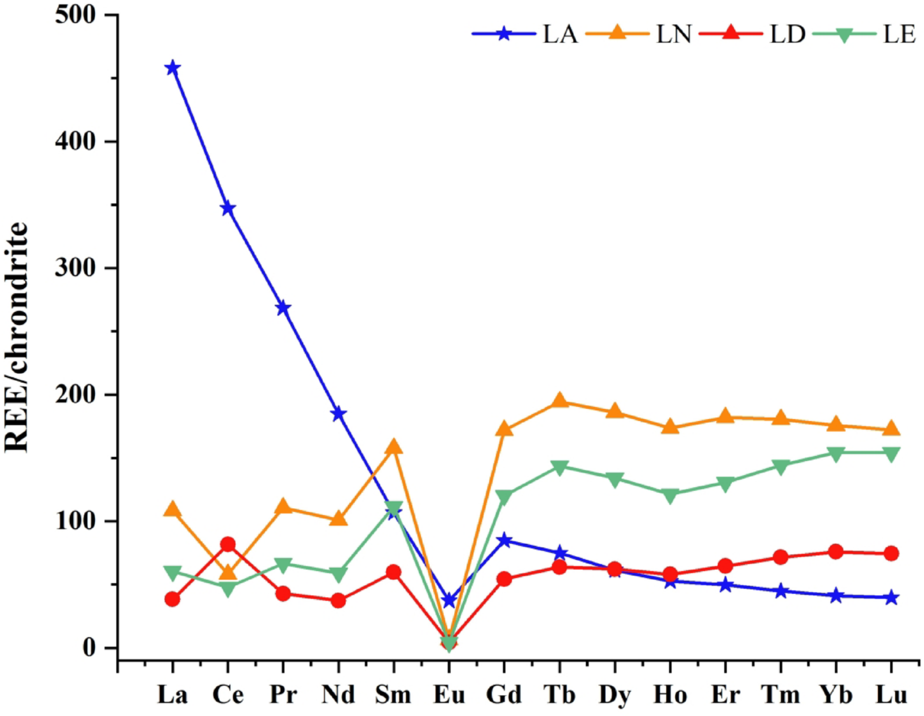

Fig. 4. Chondrite-normalized REEs distribution patterns in the unexploited soil (LA) and mining soil (LD, LN, and LE).

by La_N/Sm_N (mean of 0.64 in mining soil and 4.37 in unexploited soil) was significantly lower than the HREEs fractionation calculated with Gd_N/Yb_N (mean of 0.77 in mining soil and 2.03 in unexploited soil). Both the LA and LD samples exhibited positive anomalies, with δCe values exceeding unity ($\delta Ce > 1$). However, in the LN and LE samples, a portion of data points manifested positive Ce anomalies, and the others displayed negative Ce anomalies ($\delta Ce < 1$). In contrast, all the samples exhibited negative Eu anomalies, as characterized by δEu values ranging from 0.05 to 0.37, with an average of 0.14.

Both LREEs/HREEs and Eu/Eu* displayed extremely significant and positive correlations with La_N/Yb_N, La_N/Sm_N, and Gd_N/Yb_N ($p < 0.001$), respectively. A significantly positive correlation was also detected between LREEs/HREEs and Eu/Eu* ($p < 0.001$). The Ce/Ce* ratio was significantly and negatively correlated with Gd_N/Yb_N, indicating that an increase in Gd_N/Yb_N promoted the consumption of Ce/Ce*. pH was negatively correlated with LREEs/HREEs, Eu/Eu*, La_N/Yb_N, and La_N/Sm_N. However, organic matter was positively correlated with these variables (Fig. 6).

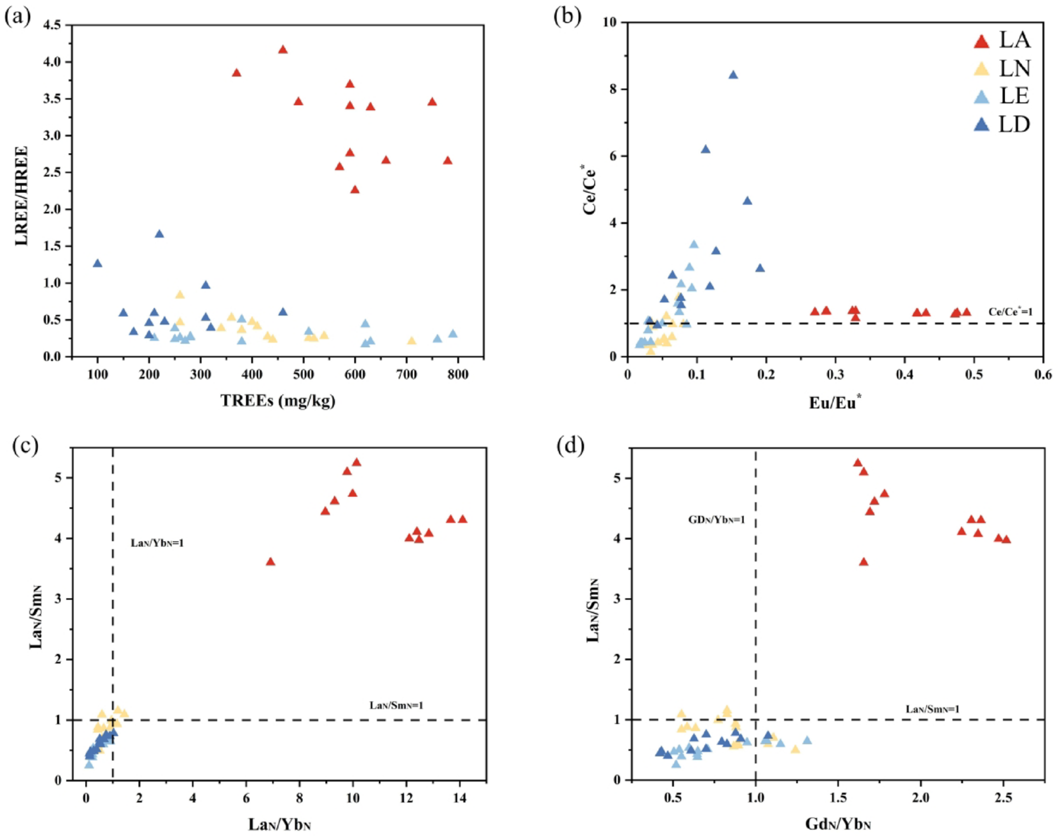

Fig. 5. The variation of TREEs and LREE/HREE (**a**), Eu/Eu* and Ce/Ce* (**b**), La_N/Yb_N and La_N/Sm_N (**c**), Gd_N/Yb_N and La_N/Sm_N (**d**) in the unexploited and mining soil samples.

Effects of soil properties on REEs characteristics

Both the mining soil and unexploited soil samples were strongly acidic, with all the pH values below 6.0. There was more organic matter and moisture content in unexploited soil than those in mining soil. However, there were no significant differences in inorganic nitrogen, TC, TN, and TS between unexploited and mining soil samples. The physicochemical properties of the 52 soil samples were shown in Table S3.

The relationships between REEs and the soil physicochemical properties were depicted in Fig. S4. Extremely significant negative correlations ($p < 0.01$) were observed between REEs (TREE, LREEs, and HREEs) and soil organic matter, as well as TN, in unexploited soil. In mining soil, the correlations between the REEs and soil pH were all significantly positive ($p < 0.01$), and no evident correlation between organic matter and REEs was detected in the mining area ($p > 0.05$).

The morphological forms of REEs were influenced by different soil properties in unexploited and mining areas, as reflected by the Mantel test (Fig. 7). In unexploited soil, organic matter, and TN appeared to have significant influences on the residual fraction (F4) ($p < 0.01$). However, in mining soils, pH was found to significantly affect all four fractions of REEs ($p < 0.05$), and organic matter displayed a significant correlation with exchangeable (F1) and residual (F4) fractions ($p < 0.05$). The moisture content was also significantly correlated with exchangeable (F1) and residual (F4) fractions.

Al and Fe chemical fractionation

The morphological distributions of Fe and Al, obtained through BCR sequential extraction, were depicted in Fig. S5 and S6. Total Al contents in mining areas and unexploited soils were 49.36–118.18 g/kg, and 44.59–109.01 g/kg, respectively. Total Fe contents in mining areas and unexploited soils were 13.22–56.87 g/kg, and 4.15–19.77 g/kg, respectively. Across all the soil samples in unexploited and mining areas, the contents and proportions of Fe and Al exchangeable fraction were lowest. These two elements were both dominated by the residual fraction, accounting for 91%–99% and 93–99%, respectively, which was significantly greater than the other fractions. The relationships between Fe, Al, and the soil physicochemical properties were shown in Fig. S7.

Discussion

Effect of mining on the geochemical behavior of REEs fractionations

Currently, there are no soil contamination or risk standards established for REEs. However, the TREEs contents of unexploited and mining soils significantly exceed the background levels of the soil in Jiangxi (211 mg kg^{-1}), China (188 mg kg^{-1})[26], and the world (154 mg kg^{-1})[7]. This indicated that the surface soils in both unexploited and

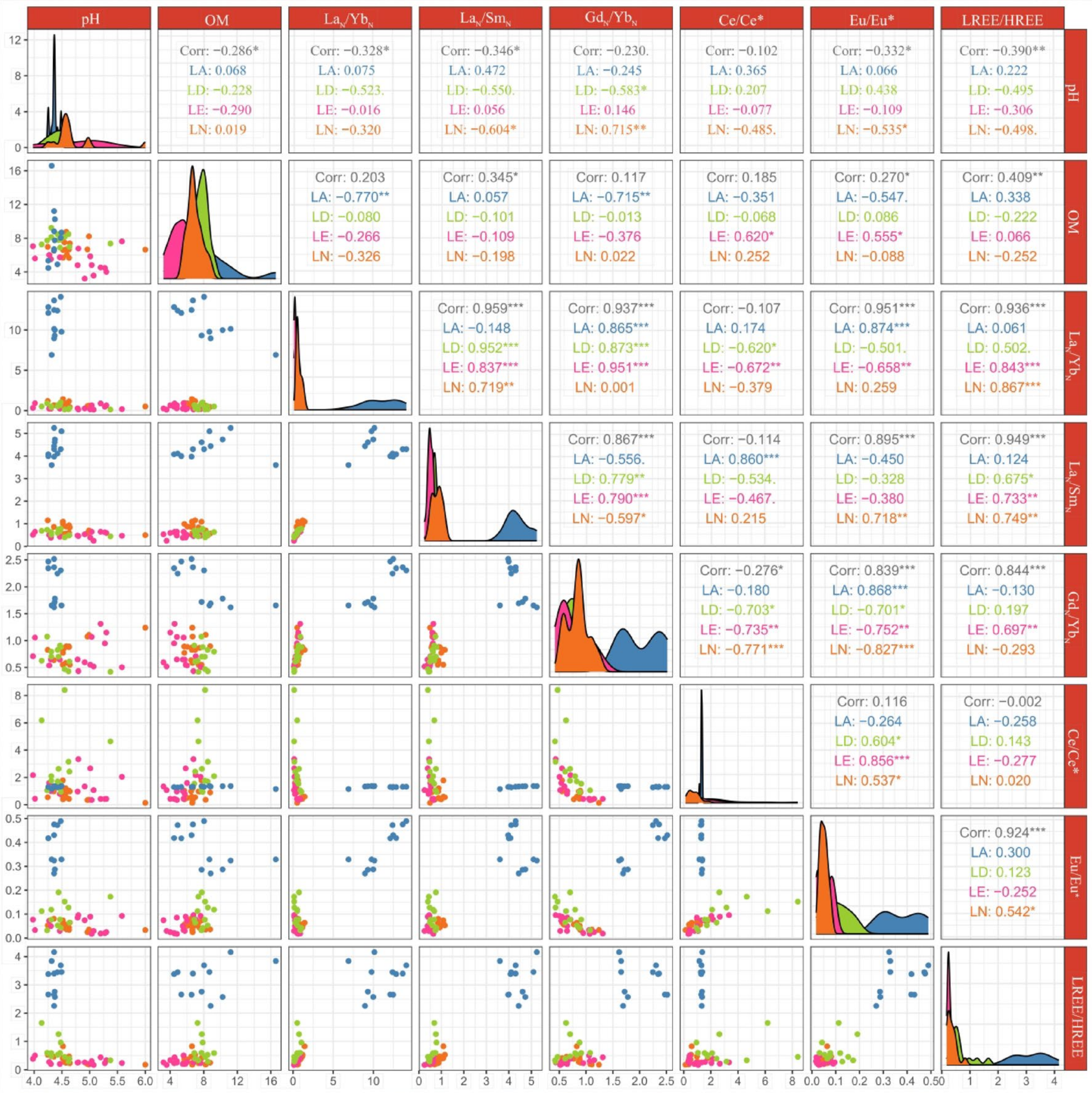

Fig. 6. Correlogram among the fractionated REEs and soil properties in all the soil samples.

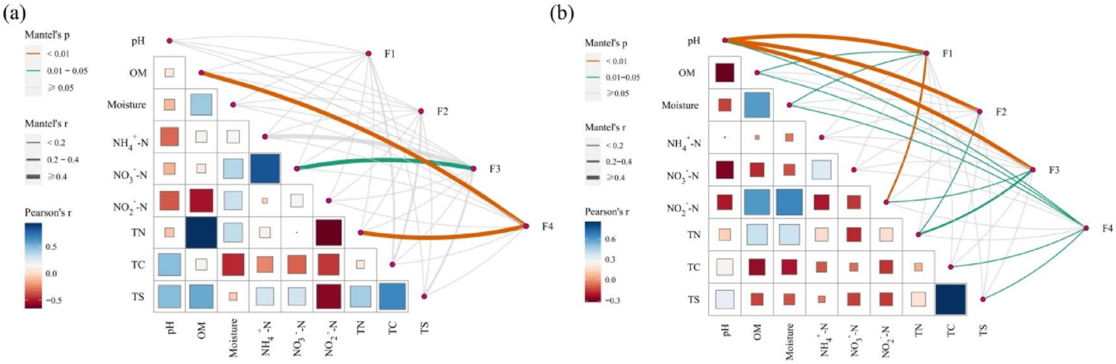

Fig. 7. Pairwise correlation matrix was shown with Mantel and partial Mantel test of REEs fractions with soil properties in unexploited soil (**a**) and mining soil (**b**). The order of environmental attributes was sorted based on the Pearson's correlation coefficients with REEs fraction by partial Mantel tests, the size of the square indicated the value of coefficient between the environment factors. OM, organic matter; F1, F2, F3 and F4 refer to REEs exchangeable, reducible, oxidizable, and residual fraction, respectively.

mining areas were enriched with high abundances of REEs. The enrichment of ionic rare earth deposits in South China is affected by several factors, such as the original parent rock, pH, weathering degree, geomorphology, particle size, clay mineral content, and soil organic matter[27]. Compared with unexploited soils, most mining soils presented lower TREEs contents. However, the TREEs of certain mining soils were remarkably higher than those of unexploited soils, which probably resulted from the drilling of injection holes in the ore body and covering it onto the surface soil.

The chemical morphological characteristics of REEs were investigated to better understand their geochemical patterns and environmental behavior. All the results of the normalized REEs fractionation patterns reflected an obvious enrichment of LREEs and significant LREEs to HREEs fractionation in unexploited soil. The LREEs/HREEs values of unexploited soil were higher than those of mining soils (Fig. 5a). According to the previous study, nearly 90% of the known REEs deposits are enriched with LREEs, with LREEs oxides accounting for more than 50% of TREEs resources[6]. In the ionic REEs mineralization process, the upper weathering crust is conducive to LREEs enrichment, as LREEs tend to accumulate in surface soils due to organic matter and Fe-Mn oxide adsorption[28,29]. At the same time, the disparity between mining and exploited soils in La_N/Yb_N and Gd_N/Yb_N values underscored the marked enrichment of HREEs over LREEs in mining areas after exploitation, especially the content of yttrium (Figs. 3a and 5c and d). HREEs were more likely to form bicarbonate and organic complexes, and then were more easily leached by the water. Thus, the middle and lower layers favor HREEs enrichment[30,31]. Before the leaching process, injection holes need to be excavated in the ore body. Therefore, the overturned middle and lower layers cover the surface soil, resulting in an increase of HREEs content in the mining topsoil. Moreover, yttrium oxides exhibit greater stability than oxides of other HREEs, and are thus less influenced by dissolution, precipitation, or other chemical reactions. The leaching process also significantly decreased the contents of LREEs (La, Ce, Nd, etc.) (Fig. 3). There findings demonstrated that mining operations changed the distributions of LREEs and HREEs in the surface soil of mining areas.

Unlike other lanthanides, Ce and Eu exhibit distinct valence states under varying redox conditions, subsequently altering their properties and abundance during soil formation[32,33]. Eu was found to be more mobile than the other REEs in the soils, whereas Ce was less mobile[34]. Consequently, Ce and Eu are fractionated from other REEs, leading to anomalies. Positive Ce and negative Eu anomalies are universally observed in the surface soil[34]. The δCe values in LA are all positive anomalies, some soil samples in the mining areas exhibit positive anomalies, whereas others display negative anomalies. These findings are consistent with most previous studies on the distribution of REEs in tailings and surrounding soils of ionic REEs deposits[35,36]. During supergene processes, distinct from other REEs, dissociated cerium rapidly oxidizes to CeO_2. CeO_2 does not migrate with surface water, but rather deposits in the humus layer and the upper part of the weathering crust, and then accumulates in the ore deposit and soil[37]. In addition, the soil type of REEs mining area is red soil. During red soil formation, hot and rainy conditions led to desilicification and allitization, which resulted in high contents of iron and aluminium oxide in the soil[38]. High iron contents in soil can also lead to the enrichment of Ce[31]. The negative Ce anomalies in some mining soil samples indicated a decrease in cerium content, which could be attributed to intense leaching activity and potentially result in severe REEs contamination in surrounding farmlands[34,39]. All the soil samples exhibited negative δEu anomalies. Eu can be easily reduced from Eu^{3+} to Eu^{2+}, and can migrate downwards, generating a negative Eu anomaly[30].

Additionally, positive correlations between Eu/Eu* and LREEs/HREEs, as well as with La_N/Yb_N, Gd_N/Yb_N, and La_N/Sm_N suggested that increases in these ratios could benefit the formation of Eu/Eu*. The negative correlation between Ce/Ce* and Gd_N/Yb_N indicated that an increase in Gd_N/Yb_N favoured the consumption of Ce/Ce* (Fig. 6). Consequently, fractionated REEs can induce further fractionation of other REEs[40].

Fractionation of REEs and their relationships with soil properties

REEs chemical speciation and bioavailability play pivotal roles in risk and hazard assessment, ecological restoration, and the management of REE-contaminated areas[10]. Chemical speciations typically determine their solubility and biological availability, which are influenced by various factors such as pH, salinity, and the presence of anions[41,42]. Before in-situ leaching, the TREEs contents of unexploited soil were higher than those of mining areas, but the residual fraction accounted for the largest proportion, and the proportion of exchangeable fraction was the smallest (Figs. 1 and 2), which implied little impact on surroundings. The residual REEs are usually present within the soil lattice of silicates, primary minerals, and secondary minerals, which are difficult to release and extract under natural conditions, and are also difficult for biota to obtain[43]. However, under strongly acidic conditions, they may migrate. During the rare earth mining process, high-concentration leaching solutions remain in the soil for an extended period, reducing the stability of residual REEs lattice structures. These structures become looser under the influence of weathering, leading to the release of REEs. These REEs are then fixed by carbonates, iron and manganese oxides, and organic matter in the form of reducible and exchangeable forms[44]. The high contents of labile REEs in mining areas were related not only to incomplete recovery of the leaching solution, but also to the presence of high concentrations of ammonium sulfate (2–4%)[16]. Soils with acid sulfate in mining areas are a source of mobile and active REEs, leading to the release of REEs[45]. Therefore, after in-situ leaching, the residual fraction remarkably decreased, and the contents and proportions of the exchangeable and reducible fractions in mining soils significantly increased. The significant correlations between exchangeable (F1), reducible (F2), and oxidizable (F3) fractions in mining soils reflected their geochemical similarity, and these fractions are also generally considered to possess potential mobility and biological availability under various environmental conditions[46]. Exchangeable fraction REEs (F1) is characterized by weak sorption and bioavailability, so it is most likely to be released into the environment through rainfall and surface runoff, and cause environmental hazards and great impacts on the surroundings. Liang reported that in unexploited areas, the exchangeable fraction of REEs accounted for 14% of TREEs, but in mining areas, this proportion increased to 44–52%[40]. These results demonstrated that human mining activities altered the soil texture and oxidation conditions, and disrupted the capacity of the soil to fix and release metals, thereby leading to changes in soil REEs forms and increasing REEs instability.

The weak correlation between soil properties and REEs chemical fractions of unexploited soil suggested that soil properties have minimal influence on the distribution and adsorption of REEs. Nevertheless, after in-situ leaching, more complex correlations between them were found in mining soils. These results implied that exploitation has disrupted the stability of REEs chemical speciations in mining areas, and the soil properties significantly affect distributions of different REEs fractions. The distribution and behaviour of REEs are influenced by soil properties, such as parent material, weathering processes, soil formation, climate, pH, redox conditions, and organic matter[47–49]. pH plays a crucial role in controlling the mobility of REEs in environments, and exhibited a significant negative correlation with the migration rate of REEs. Because a relatively high pH significantly enhances the absorption of REEs, thus reducing their migration rate[39]. In the unexploited soils of this study, no significant correlation was detected between pH and REEs, or between pH and different chemical fractions of REEs. Similar results have been reported in the soils of coal mines in Brazil and other regions[39,50]. In the mining area, pH was significantly and positively correlated not only with TREE, but also with four different chemical fractions of REEs. This discrepancy might arise from the small pH variation range (4.1–5.3) in mining soils, which were strongly acidic and exhibited limited variation. This pH range is similar to that of red soils in southern China, where over-acidified soil conditions may mask the influence of soil pH on the distribution and behavior of REEs[34].

The combinations of REEs and soil organic matter are influenced by the type, composition, and content of organic matter, as well as the soil pH and redox conditions[51]. Organic matter exhibited a significant negative correlation with REEs in unexploited soil, possibly due to the formation of complexes/chelates[52]. The low organic matter content in mining soil may lead to weak adsorption of REEs, so there is no significant correlation was detected. Moisture is a driving force for REEs displacement, as increased humidity enhances microbial activity[53]disrupting rare earth phosphate compounds and promoting the release of REEs[54]. The significant correlations between moisture content and F1/F4 would be related to the REEs chemical morphological changes caused by exploitation. In the ammonium sulfate leaching process, potential leakage of impermeable layers, inadequate collection systems, and high nitrogen contents not only results in the retention of a significant amount of nitrogen, but also traps sulfate ions in soil, concealing the relationship between TN and REEs[55]. Furthermore, there were extremely high outliers in TN and TC contents in some of the soil samples (e.g., TN values of LE1 and LN13, TC values of LD7 and LD8). This may be due to the presence of bird feces or calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], or other carbonate minerals in the soil samples.

Effects of mining on Fe and Al morphology

Jiangxi is known as the "Red Soil Region" due to its iron-rich soil, which contains iron-aluminum oxides or carbonate substances. The soil in this region is slightly acidic, primarily because of the transformation of Al into active forms. Aluminum and iron ions are major impurities in leaching solutions of ion-absorbed rare earth ores[56]. Therefore, the soil samples contained high contents of Fe and Al elements. The predominant chemical speciation of Al and Fe elements in all the soil samples from both the unexploited and mining areas was the residual fraction, which was more stable, less reactive, and significantly more abundant content than the other three fractions. The predominant residual fraction and lower content of labile fractions might result in no significant correlation between the fractions of Fe/Al elements and the fractions of REEs.

Effect of REEs on the environment of mining areas

Soil formation processes and human activities significantly influence REEs concentrations and speciation. In undisturbed environments, the residual REEs dominate, followed by the oxidizable and reducible fractions, with the lowest content of exchangeable REEs. These distributions primarily result from pedogenesis processes and parent rock weathering[16,57]which control REEs release and fixation. Although the TREEs content may be high in unexploited soil, their limited mobility minimizes environmental and human health impacts. Mining activities alter soil physicochemical properties and redox conditions, enhancing REEs mobility and bioavailability. Although TREEs concentrations often decrease after mining, the content and proportion of exchangeable and reducible REEs increase. Elevated REEs exchangeable fraction may inhibit microbial activity and soil enzyme functions[58]disrupting critical biogeochemical cycles. During the process of plant restoration, REEs in bioavailable forms can uptake by plants, potentially disrupting nutrient absorption and causing oxidative stress[59]resulting in slow growth. Moreover, the increased bioavailability of REEs poses ecological risks through leaching or runoff, and increases human exposure through contaminated crops, dust inhalation, or water sources[60,61]which could cause lung and hepatocyte toxicity, and accumulation toxicity[7].

Traditional monitoring focusing solely on TREEs content significantly underestimates risk in mining areas. So, routine monitoring programs in and around mining areas should mandatorily include speciation analysis (e.g., BCR sequential extraction) to quantify the bioavailable (exchangeable) and potentially mobilizable (reducible) fractions. This provides a true picture of environmental hazard. In the process of vegetation restoration in mining areas, targeted selection of plants that can adsorption/fix REEs will reduce their bioavailability and mobility. Our findings provide the critical scientific basis for designing effective remediation strategies, improving monitoring methods, and guiding mine waste management. We also emphasize the necessity of post-mining remediation (e.g., plant stabilization, soil amendment) and long-term monitoring to mitigate ecosystem risks and protect human health.

Conclusion

This study systematically analyzed the contents, distributions, and chemical speciations of REEs in unexploited soils and mining soils in southern Jiangxi Province. The results revealed presented positive Ce and negative Eu anomalies in all the soil samples, with lower TREEs contents in mining soils compared to unexploited soils. Mining activities not only reduced the content of TREEs, but also altered the LREEs/HREEs distributions and chemical speciations in mining areas. The residual fraction dominated in unexploited soils, and the proportions of the exchangeable fraction were the lowest. Mining activities significntly decreased the contents and proportions of the residual fractions, while increased the exchangeable and reducible REEs. This alteration enhanced REEs instability, mobility, and bioavailability, probably becoming potential environmental risks. These findings demonstrate that mining activities have the potential to modify the distribution and geochemical behavior of REEs, and highlight the need for stricter environmental management in mining areas to mitigate REEs contamination. However, the mechanisms driving REE fractionation and speciation changes during mining process require further investigation. Remediation strategies and regulatory measures should be explored to protect ecosystems and human health.

Data availability

The data will be made available from the corresponding author upon reasonable request.

Received: 28 April 2025; Accepted: 24 July 2025

References

1. Chakhmouradian, A. & Wall, F. Rare Earth elements: minerals, mines, magnets (and more). *Elements* **8**, 333–340 (2012).
2. Migaszewski, Z. M. & Galuszka, A. The characteristics, occurrence, and geochemical behavior of rare Earth elements in the environment: A review. *Crit. Rev. Environ. Sci. Technol.* **45** (5), 429–471 (2015).
3. Ramos, S. J. et al. Rare Earth elements in the soil environment. *Curr. Pollution Rep.* **2** (1), 28–50 (2016).
4. Tan, Q. Y., Li, J. H. & Zeng, X. L. Rare Earth elements recovery from waste fluorescent lamps: A review. *Crit. Rev. Environ. Sci. Technol.* **45** (7), 749–776 (2015).
5. Xie, F., Zhang, T. A., Dreisinger, D. & Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Min. Eng.* **56**, 10–28 (2014).
6. Li, Y. H. M., Zhao, W. W. & Zhou, M. F. Nature of parent rocks, mineralization styles and ore genesis of regolith-hosted REE deposits in South china: an integrated genetic model. *J. Asian Earth Sci.* **148**, 65–95 (2017).
7. Wang, Y. Y. et al. Environmental risk assessment of the potential chemical time bomb of ion-adsorption type rare Earth elements in urban areas. *Sci. Total Environ.* **822**, 153305 (2022).
8. Liu, S., Huang, Y., Zhu, X. & Liu, X. Environmental effects of ion-absorbed type rare Earth extraction on the water and soil in mining area and its peripheral areas. *Environ. Sci. Technol.* **38** (6), 8 (2015). (in Chinese).
9. Yang, X. J. et al. China's ion-adsorption rare Earth resources, mining consequences and preservation. *Environ. Dev.* **8**, 131–136 (2013).
10. Khan, A. M., Abu Bakar, N. K., Abu Bakar, A. F. & Ashraf, M. A. Chemical speciation and bioavailability of rare Earth elements (REEs) in the ecosystem: a review. *Environ. Sci. Pollut Res.* **24** (29), 22764–22789 (2017).
11. Li, W. S. et al. Abundance, Spatial variation, and sources of rare Earth elements in soils around ion-adsorbed rare Earth mining areas. *Environ. Pollut.* **313**, 120099 (2022).
12. Tayeh, B. et al. Recycling of mine tailings for the geopolymers production: A systematic review. *Case Stud. Constr. Mater.* **16**, e00933 (2022).
13. Chao, Y. Q. et al. Structure, variation, and co-occurrence of soil microbial communities in abandoned sites of a rare Earth elements mine. *Environ. Sci. Technol.* **50** (21), 11481–11490 (2016).
14. Liu, J. J. et al. Exploitation alters microbial community and its co-occurrence patterns in ionic rare Earth mining sites. *Sci. Total Environ.* **898**, 165532 (2023).
15. Jin, S., Huang, Y., Hu, Y., Qiao, M. & Xu, F. Rare Earth elements content and health risk assessment of soil and crops in typical rare Earth mine area in Jiangxi Province. *Acta Sci. Circum.* **34** (12), 3084–3093 (2014).
16. Ou, X. L. et al. Redistribution and chemical speciation of rare Earth elements in an ion- adsorption rare Earth tailing, Southern China. *Sci. Total Environ.* **821**, 153369 (2022).
17. Lu, S. et al. Research on the ecological risk of heavy metals in the soil around a Pb–Zn mine in the Huize county, China. *Chin. J. Geochem.* **34**, 540–549 (2015).
18. Meng, J., Tao, M. M., Wang, L. L., Liu, X. M. & Xu, J. M. Changes in heavy metal bioavailability and speciation from a Pb-Zn mining soil amended with biochars from co-pyrolysis of rice straw and swine manure. *Sci. Total Environ.* **633**, 300–307 (2018).
19. Li, Z. Y., Ma, Z. W., van der Kuijp, T. J., Yuan, Z. W. & Huang, L. A review of soil heavy metal pollution from mines in china: pollution and health risk assessment. *Sci. Total Environ.* **468**, 843–853 (2014).
20. Chen, L. W. et al. Speciation, fate and transport, and ecological risks of Cu, Pb, and Zn in tailings from Huogeqi copper mine, Inner Mongolia, China. *J. Chem.* 2340542, (2018). (2018) (1).
21. Zhang, J. L. et al. Speciation analysis and pollution assessment of heavy metals in farmland soil of a typical mining area: A case study of Dachang Tin polymetallic ore, Guangxi. *Appl. Sci. -Basel.* **13** (2), 708 (2023).
22. Zhang, X., Yang, H. H. & Cui, Z. J. Migration and speciation of heavy metal in salinized mine tailings affected by iron mining. *Water Sci. Technol.* **76** (7), 1867–1874 (2017).
23. Cunha, C. S. M., da Silva, Y. & Escobar, M. E. O. Do nascime, C. W. A. Spatial variability and geochemistry of rare Earth elements in soils from the largest uranium-phosphate deposit of Brazil. *Environ. Geochem. Health*. **40** (4), 1629–1643 (2018).
24. Compton, J. S., White, R. A. & Smith, M. Rare Earth element behavior in soils and salt Pan sediments of a semi-arid granitic terrain in the Western cape, South Africa. *Chem. Geol.* **201** (3–4), 239–255 (2003).
25. Rabiet, M., Brissaud, F., Seidel, J. L., Pistre, S. & Elbaz-Poulichet, F. Positive gadolinium anomalies in wastewater treatment plant effluents and aquatic environment in the Herault watershed (South France). *Chemosphere* **75** (8), 1057–1064 (2009).
26. Gwenzi, W. et al. Sources, behaviour, and environmental and human health risks of high-technology rare Earth elements as emerging contaminants. *Sci. Total Environ.* **636**, 299–313 (2018).
27. Chen, H. X., Chen, L. K., Zhang, L. & Guo, M. Spatial heterogeneity of rare Earth elements: implications for the topsoil of regional ion-adsorption type rare Earth deposit areas in Southern China. *Minerals* **13** (6), 784 (2023).
28. Braun, J. J. et al. REY-Th-U dynamics in the critical zone: combined influence of reactive bedrock accessory minerals, authigenic phases, and hydrological sorting (Mule hole watershed, South India). *Geochem. Geophy Geosy*. **19** (5), 1611–1635 (2018).
29. Li, M. Y. H., Zhou, M. F. & Williams-Jones, A. E. The genesis of regolith-hosted heavy rare Earth element deposits: insights from the world-class Zudong deposit in Jiangxi province, South China. *Econ. Geol.* **114** (3), 541–568 (2019).
30. Lin, Z. L., Wei, G. L., Zhang, J. L., Liang, X. L. & Huang, G. Q. Origin and distribution of rare Earth elements (REEs) in the soils of Meizhou city, Southern China with high abundance of regolith-hosted REEs. *Appl. Geochem.* **147**, 105514 (2022).

31. Yuan, Y. Y. et al. Effects of topography and soil properties on the distribution and fractionation of REEs in topsoil: A case study in Sichuan basin, China. *Sci. Total Environ.* **791**, 148404 (2021).
32. Lidman, F., Laudon, H., Köhler, S. & Taberman & Eu anomalies in soils and soil water from a boreal hillslope transect - A tracer for holocene lanthanide transport? *Geochim. Cosmochim. Acta*. **267**, 147–163 (2019).
33. Rogova, O. B., Fedotov, P. S., Dzhenloda, R. K. & Karandashev, V. K. Fractionation and fixation of rare Earth elements in soils: effect of spiking with lanthanum, cerium, and neodymium chlorides. *J. Rare Earths*. **40** (1), 143–152 (2022).
34. Chang, C. et al. Fractionation characteristics of rare Earth elements (REEs) linked with secondary fe, mn, and al minerals in soils. *Acta Geochim.* **35** (4), 11 (2016).
35. Chen, B. H., Wei, X. H., Huang, Z. G. & Zhou, Y. Z. Cerium anomalies in supergene geological bodies and its effecting factors. *Chin. Rare Earths*. **28** (4), 79–83 (2007). (in Chinese).
36. Zhou, W. X., Han, G. L., Liu, M., Song, C. & Li, X. Q. Geochemical distribution characteristics of rare Earth elements in different soil profiles in mun river basin, Northeast Thailand. *Sustainability* **12** (2), 457 (2020).
37. Hua, G., Huang, T. L., Huang, Z. S. & Zhou, W. J. Mining situation and geochemistry characteristics of three ion adsorption rare-earth deposit in Guangdong Province. *Rock. Mineral. Anal.* **46** (10), 1177–1201 (2014). (in Chinese).
38. Guo, J. X. et al. Inversion of soil properties in rare Earth mining areas (southern jiangxi, China) based on visible-near-infrared spectroscopy. *J. Soils Sediments*. **22** (9), 2406–2421 (2022).
39. Liang, T., Li, K. X. & Wang, L. Q. State of rare Earth elements in different environmental components in mining areas of China. *Environ. Monit. Assess.* **186** (3), 1499–1513 (2014).
40. Zerizghi, T. et al. Rare Earth elements in soil around coal mining and utilization: contamination, characteristics, and effect of soil physicochemical properties. *Environ. Pollut*. **331**, 121788 (2023).
41. Ashraf, M. A., Maah, M. J., Yusoff, I. & Ghararibreza, M. Speciation of heavy metals in the surface waters of a former Tin mining catchment. *Chem. Speciat. Bioavailab.* **24** (1), 1–12 (2012).
42. Han, K. Effect of anions on the solubility of rare Earth element-bearing minerals in acids. *Min. Metall. Explor.* **36** (1), 215–225 (2019).
43. Chang, C., Song, C. S., Beckford, H. O., Wang, S. J. & Ji, H. B. Behaviors of REEs during pedogenetic processes in the karst areas of Southwest China. *J. Asian Earth Sci.* **185**, 104023 (2019).
44. Peng, G. Speciation analysis of rare Earth elements in soil. *Chin. J. Anal. Chem.* **36**, 1483–1487 (2008).
45. Fernández-Caliani, J. C., Barba-Brioso, C. & De la Rosa, J. D. Mobility and speciation of rare Earth elements in acid minesoils and geochemical implications for river waters in the Southwestern Iberian margin. *Geoderma* **149** (3–4), 393–401 (2009).
46. Palansooriya, K. N. et al. Soil amendments for immobilization of potentially toxic elements in contaminated soils: A critical review. *Environ. Int.* **134**, 105046 (2020).
47. Cao, X., Chen, Y., Wang, X. & Deng, X. Effects of redox potential and pH value on the release of rare Earth elements from soil. *Chemosphere* **44** (4), 655–661 (2001).
48. Mihajlovic, J. & Rinklebe, J. Rare Earth elements in German soils - A review. *Chemosphere* **205**, 514–523 (2018).
49. Mwewa, B., Tadie, M., Ndlovu, S., Simate, G. S. & Matinde, E. Recovery of rare Earth elements from acid mine drainage: A review of the extraction methods. *J. Environ. Chem. Eng.* **10** (3), 107704 (2022).
50. Galhardi, J. A., Leles, B. P., de Mello, J. W. V. & Wilkinson, K. J. Bioavailability of trace metals and rare Earth elements (REE) from the tropical soils of a coal mining area. *Sci. Total Environ.* **717**, 134484 (2020).
51. Laveuf, C. & Cornu, S. A review on the potentiality of rare rarth elements to trace pedogenetic processes. *Geoderma* **154** (1–2), 1–12 (2009).
52. Davranche, M. et al. Biogeochemical factors affecting rare Earth element distribution in shallow wetland groundwater. *Aquat. Geochem.* **21** (2–4), 197–215 (2015).
53. Caspari, T., Bäumler, R., Norbu, C., Tshering, K. & Baillie, I. Geochemical investigation of soils developed in different lithologies in bhutan, Eastern Himalayas. *Geoderma* **136** (1–2), 436–458 (2006).
54. Liang, J. L. et al. Novel phosphate-solubilizing bacteria enhance soil phosphorus cycling following ecological restoration of land degraded by mining. *ISME J.* **14** (6), 1600–1613 (2020).
55. Fernandes, C. C. et al. Bacterial communities in mining soils and surrounding areas under regeneration process in a former ore mine. *Braz J. Microbiol.* **49** (3), 489–502 (2018).
56. Qiu, T. S., Fang, X. H., Wu, H. Q., Zeng, Q. H. & Zhu, D. M. Leaching behaviors of iron and aluminum elements of ion-absorbed-rare-earth ore with a new impurity depressant. *T Nonferr Metal Soc.* **24** (9), 2986–2990 (2014).
57. Durn, G., Perkovic, I., Stummeyer, J., Ottner, F. & Mileusnic, M. Differences in the behaviour of trace and rare-earth elements in oxidizing and reducing soil environments: case study of Terra Rossa soils and cretaceous palaeosols from the Istrian Peninsula. *Croatia Chemosphere*. **283**, 131286 (2021).
58. Xiao, C. Q. et al. Performance changes in the anammox process under the stress of rare-earth element Ce(III) and the evolution of microbial community and functional genes. *Bioresour Technol.* **384**, 129349 (2023).
59. Thomas, P. J., Carpenter, D., Boutin, C. & Allison, J. E. Rare Earth elements (REEs): effects on germination and growth of selected crop and native plant species. *Chemosphere* **96**, 57–66 (2014).
60. Ferreira, M. D. et al. Human health risk assessment and geochemical mobility of rare Earth elements in Amazon soils. *Sci. Total Environ.* **806** (2), 151191 (2022).
61. Li, X. F., Chen, Z. B., Chen, Z. Q. & Zhang, Y. H. A human health risk assessment of rare Earth elements in soil and vegetables from a mining area in Fujian province, Southeast China. *Chemosphere* **93** (6), 1240–1246 (2013).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 52304187) and the Natural Science Foundation of Jiangxi Province (20224BAB203041).

Author contributions

Z.W. Writing-original draft preparation, visualization, data curation, conceptualization. J.L. Conceptualization, methodology, supervision, writing-reviewing and editing, funding acquisition. C.L. Investigation, resources, validation, formal analysis. W.L. and W.W. Supervision, writing - review and editing. All authors reviewed the manuscript.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-025-13513-2.

Correspondence and requests for materials should be addressed to J.L.

Reprints and permissions information is available at www.nature.com/reprints.

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

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/.

© The Author(s) 2025