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Geochemical Characteristics of Soil Rare Earth Elements within Spontaneous Combustion Coalfields of Rujigou Coal Mine

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Abstract: (1) Background: The spontaneous combustion of coal (SCC) not only consumes huge amounts of coal resources but also causes environmental degradation. Rare earth elements (REE) can be taken as an effective indicator to evaluate the environmental effects of SCC. Coal in the Rujigou Mine has been spontaneously combusting for hundreds of years. (2) Methods: The geochemical properties of REE and major elements in the soil of the Rujigou coal mine are methodically examined to reveal the environmental effects of SCC. (3) Results: Soil REE concentration in the Rujigou mine is 216.09 mg/kg, and there is an enrichment of light rare earth elements (LREE) and a depletion of heavy rare earth elements (HREE), LREE/HREE in Rujigou mine was 5.52. The spontaneous combustion of coal could change the vertical distribution of REE, which is conducive to the enrichment of LREE. According to the Eu anomaly and $\delta\text{Ce}/\delta\text{Eu}$, the source of material in this mine may be derived from the terrigenous clastic rock controlled by weak reduction. Aluminum and titanium have similar geochemical behavior to REE, especially LREE. The concentration of sulfur is negatively correlated with REE, especially HREE. Calcium, sodium, and magnesium all had a negative correlation with LREE. (4) Conclusions: The spontaneous combustion of coal can lead to the fractionation of light and heavy rare earth elements, resulting in the enrichment of LREE and depletion of HREE.

Keywords: rare earth elements; spontaneous combustion coalfield; soil profile; enrichment and depletion



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1. Introduction

Nowadays, the energy structure is still dominated by coal worldwide [1]. The persistently high demand for coal has led to continued mining, which has resulted in a series of environmental issues. One of the most significant disasters in coal mines is coal spontaneous combustion, which not only affects the safe and effective mining of coal but also poses a potential risk to the ecology and leads to serious environmental pollution [2–4]. Spontaneous combustion is a complex physicochemical phenomenon associated with many internal and external factors. There are many hypotheses about the mechanism of coal spontaneous combustion, including free radical reactions, pyrite action, phenolization, bacterial action, coal–oxygen recombination theory, etc. [5–7], of which the coal–oxygen recombination theory has been widely accepted. It claims that coal spontaneous combustion often occurs in underground coal seams and is mostly ignited by self-heating [8]. After coal mining, the ground cracks serve as an oxygen supply channel for coal and ash that remains underground, which creates favorable ventilation conditions for the coal pillar, roof, and crushed coal that is left over in the inner goaf [9]. The exterior coal seam that is exposed to the air is gradually oxidized and the heat is released. With the continuous oxidation and raising of ambient temperature, the coal seam eventually approaches its ignition point and begins to burn [10–13].

The spontaneous combustion of coal has been observed all over the world [14–16]. In China, the spontaneous combustion of coal has been reported in more than 90% of coal

mines among 130 large- and medium-sized mining areas [13,17–20]. The hazard poses a direct threat to human life and property, results in the wastage of non-renewable resources, generates residue and wastewater, emits exhaust gases, and alters soil moisture dynamic mechanisms as well as the physical and chemical properties of the soil. The spontaneous combustion of coal causes a redistribution of soil trace elements, which is not conducive to the regional ecological balance [16,21–23].

Rare earth elements (REE) are a group of 17 elements with unique chemical properties and extensive uses, including Scandium (Sc), Yttrium (Y), and the lanthanide series elements: Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu) [24,25]. REEs are primarily from natural sources; these are generally employed to identify the source of soil materials and are regarded as an indicator to monitor the changes in soil conditions. Their concentration is related to the mineral composition and is also influenced by geological processes such as metamorphism and tectonic movements [26]. Chemical weathering plays a crucial role in determining the distribution patterns of REEs in soil, sediment, and rock [27]. REEs typically exist as trivalent cations in carbonates, phosphates, silicates, and oxides [28]; among these, Ce and Eu may assume other valence states.

Affected by mining activities, the physicochemical properties of soil in mining areas are complicated, particularly in mines where the spontaneous combustion of coal occurs. REEs can be employed as environmental tracers of soil-forming processes. Under normal circumstances, REEs naturally exist in an environment with a low concentration [29]. However, due to the ubiquitous anthropogenic activities, the original physicochemical properties of soil are changed, and the evaluation of REE distribution patterns, especially those relevant to estimating possible anomalies of natural concentrations, is of great significance [30]. The chemical properties of REE in the soil may reflect the regional geological conditions and record the progress of coal spontaneous combustion.

Rujigou Coal Mine, located in north-central Helan Mountain, was rich in high-quality anthracite; however, the spontaneous combustion of coal in this mine has a history of hundreds of years. The spontaneous combustion of coal in this mining area has led to a mass of coal loss and an unquantifiable economic loss annually [10]. The concentration of REE in the soil of the Rujigou mining area and the mine periphery area was analyzed by on-site sampling and laboratory tests. The effects of mining and coal spontaneous combustion on the soil environment were also explored by analyzing the differences in soil REE between concentrations of mining areas and background areas and between the spontaneous combustion coalfields where they were occurring and extinguished.

2. Overview of the Study Area and Explanation of Materials

2.1. Overview of the Rujigou Mining Area

Rujigou Coal Mine is located in the north-central Helan Mountains under the jurisdiction of Shizuishan, Ningxia Hui Autonomous Region and adjacent to the Alxa Left Banner of Inner Mongolia Autonomous Region. It belongs to a typical temperate continental climate characterized by a low annual precipitation of 200 mm and a wide annual temperature range of 50 °C. The main soil type is sierozem, which is alkaline, low in nutrients, and low in humus and organic matter. Vegetation coverage in this area is 10% and mainly includes Chenopodiaceae, Asteraceae, Poaceae, and Fabaceae [31]. The coal deposits are based on the Archeozoic Helan Mountain Group and are covered from bottom to top by Cambrian, Ordovician, Carboniferous, Permian, Jurassic, and Quaternary strata. The coal-bearing strata are mostly dominated by the Middle Jurassic Yanan Group, with nine coal-bearing seams demonstrating a thinning trend from southeast to northwest [32]. Generally, the Rujigou mining area is a small basin of Jurassic intermontane half-graben in the middle part of the Helan Mountain fault-fold belt [33].

This coal mine is integrated with the Rujigou Coal Mine, Baijigou Coal Mine, and Dafeng Coal Mine. Coal in this mine is mostly in the Jurassic Yanan Formation strata, and

all of them are anthracite, essentially characterized by relatively shallow buried depth, low ash, low sulfur, low phosphorus, high caloric, high specific resistance, and high chemical activity [34]. Mining activities in this area can be traced back to centuries ago, and the annual production of coal resources was about 4.5 million tons. However, the spontaneous combustion of coal has been detected in Baijigou, Nanyi, Erdaoling, and Shitanjing coalfields, and the spontaneous combustion area is even up to 3.95 square kilometers. Annually, nearly a million tons of coal in this mine are directly destroyed by spontaneous combustion.

2.2. Sample Preparation and Chemical Assay

According to the surface temperature data retrieved by Landsat for nearly 30 years [35], the temperature anomalies in the Rujigou mining area were extracted, and the spontaneous combustion coal field was confirmed through field investigation. According to the results, the mining area (MA) can be divided into three sections: new spontaneous combustion coalfield (NSCF), sustained spontaneous combustion coalfield (SSCF), and extinguishing spontaneous combustion coal field (ESCF). Meanwhile, the periphery of the mining area (PMA) was selected as a contrast to investigating the influences of coal mining activities and spontaneous combustion on the soil in the mining area.

A total of 50 sample points were selected in the Rujigou mine area in July 2022 (Figure 1), including 16 in NSCF and SSCF, respectively, 13 in ESCF, and 5 in PMA. At the same time, three soil profiles were dug and 18 samples were collected at the depths of 5, 20, 40, 60, 80, and 100 cm in NSCF, SSCF, and ESCF. The soil samples were placed in an oven to dry at 60 °C and turned into powder via an agate mortar, and then they were filtered through an 80-mesh sieve and stored in sample bags for testing. The mass fractions of REEs and major elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) at Aoshi Analysis and Testing Co., LTD, Guangzhou, China.

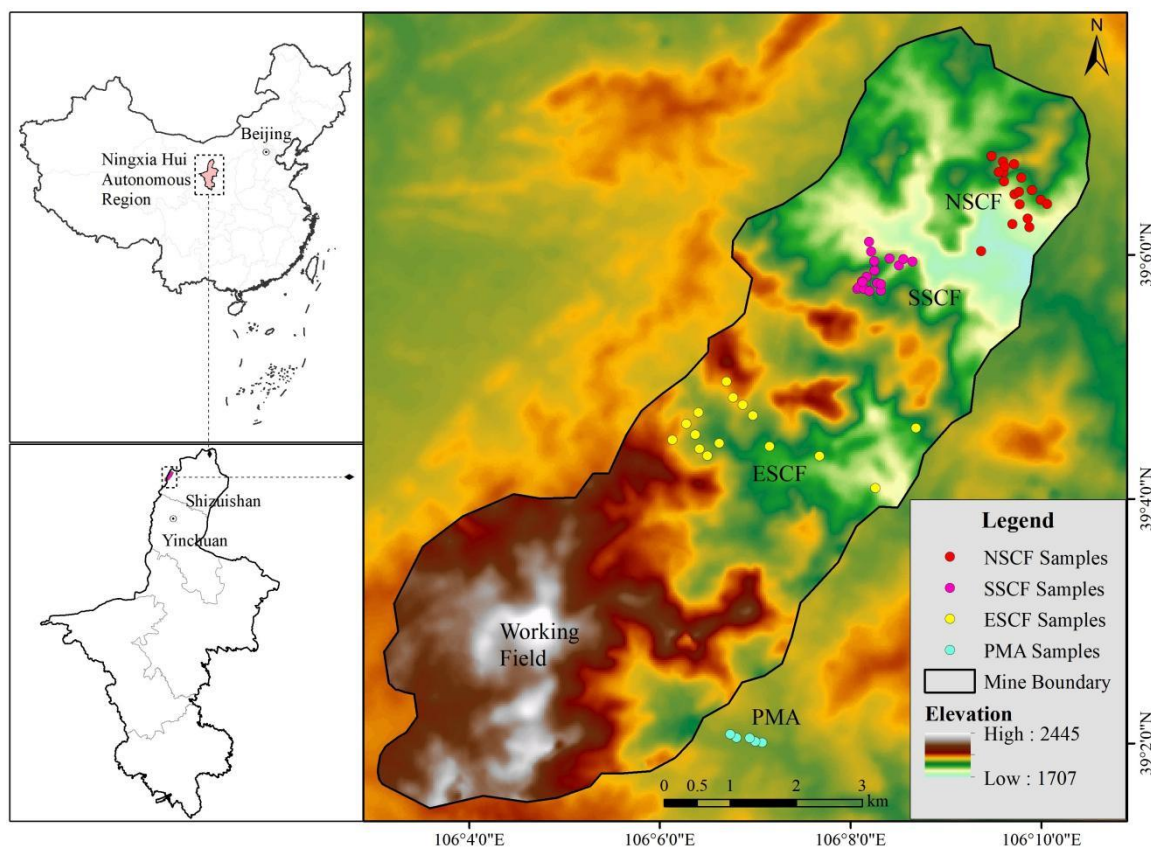


Figure 1. Location and sample distribution of the Rujigou Coal Mine.

3. Results

3.1. REE Concentration of Mine Area and Its Periphery

The mean concentration of soil REE in MA ranged from 0.31 to 86.06 mg/kg (Figure 2a), among which Ce had the highest value of 86.06 mg/kg. Lanthanum, Nd, and Y possess concentrations of 43.10, 35.98, and 18.92 mg/kg, respectively. Praseodymium, Sm, Gd, Dy, Er, Yb, and Eu concentrations were in descending order with values between 1 and 10 mg/kg, and Ho, Tb, Lu, and Tm were below 1 mg/kg. The coefficient of variation of each element in MA was substantially higher than PMA (Figure 2b), which indicated a great dimensional difference among the sample points in MA. Σ REE (sum of all rare earth elements) in MA was equal to 216.09 mg/kg (ranged between 142.20 and 348.18 mg/kg), of which Σ LREE (sum of all light rare earth elements: La, Ce, Pr, Nd, Sm, and Eu) makes up 84.55% with a value of 182.71 mg/kg (variation from about 116.60 to 292.59 mg/kg), while Σ HREE (sum of all heavy rare earth elements: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) constitutes 15.45% with a value of 33.38 mg/kg (variation in the range of 21.35 to 55.59 mg/kg).

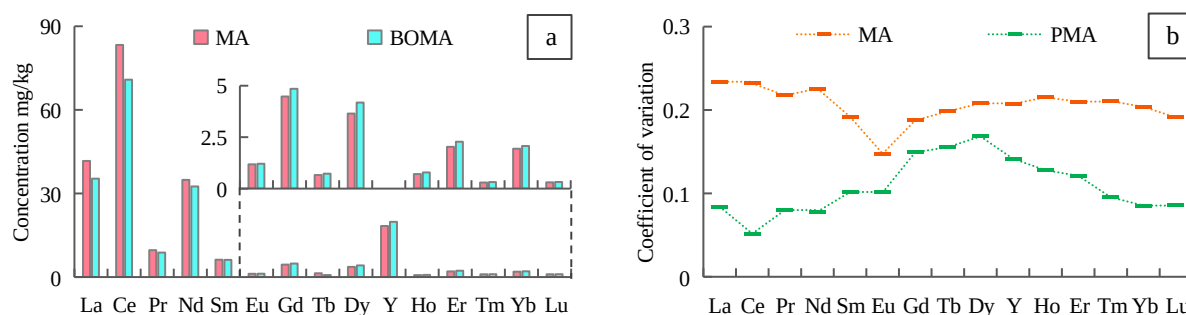


Figure 2. Characteristics of various REEs in the soil of MA and PMA: (a) concentration, (b) coefficient of variation.

The specific value of LREE/HREE was 5.52, which indicated that LREE was enriched. The concentration of REE in PMA showed the same characteristics as MA. In descending order, REE concentrations in PMA soil were as follows: Ce > La > Nd > Y > Pr > Sm > Gd > Dy > Er > Yb > Eu > Ho > Tb > Lu > Tm. It should be noted that every LREE in PMA was lower than MA except Eu, but every HREE in PMA was higher than MA. The sum of REEs in PMA was 190.20 mg/kg, ranging from 172.05 to 208.42 mg/kg. The sums of LREE and HREE were 154.85 mg/kg and 35.35 mg/kg, respectively, which, in order, occupied 81.41% and 18.59% of Σ REE. The ratio of LREE/HREE was 4.42, which was lower than MA. Compared to MA, Σ REE was lower in PMA, but Σ HREE was slightly higher with a different value of 1.98 mg/kg.

To further understand the effect of coal spontaneous combustion on REE in mine soil, samples in NSCF, SSCF, and ESCF were analyzed (Figure 3). The differences in REE concentration in various coalfields are presented as SSCF (224.75 mg/kg), greater than NSCF (222.24 mg/kg) and higher than ESCF (197.89 mg/kg). There was little discrepancy between SSCF and NSCF. Σ REE, Σ LREE, and Σ HREE in SSCF were obtained as 224.75, 191.23, and 33.52 mg/kg, in which all these values are slightly higher than that in NSCF; the difference values were 2.51, 1.94, and 0.57 mg/kg, respectively. The LREE/HREE values of SSCF were close to the values of NSCF (i.e., 5.78 and 5.76, respectively). The REE concentration of ESCF was estimated to be 197.89 mg/kg, which was much lower than those of SSCF and NSCF but close to PMA (190.20 mg/kg), whereas HREE, here, was obtained as 33.75 mg/kg, slightly higher than other two coalfields. The ratios of Σ HREE to Σ REE in NSCF, SSCF, and ESCF were 14.83%, 14.91%, and 17.06%, respectively, which were all lower than that of PMA (18.59%). Therefore, it was inferred that coal combustion contributes to LREE enrichment, but HREE may be deficient during this process.

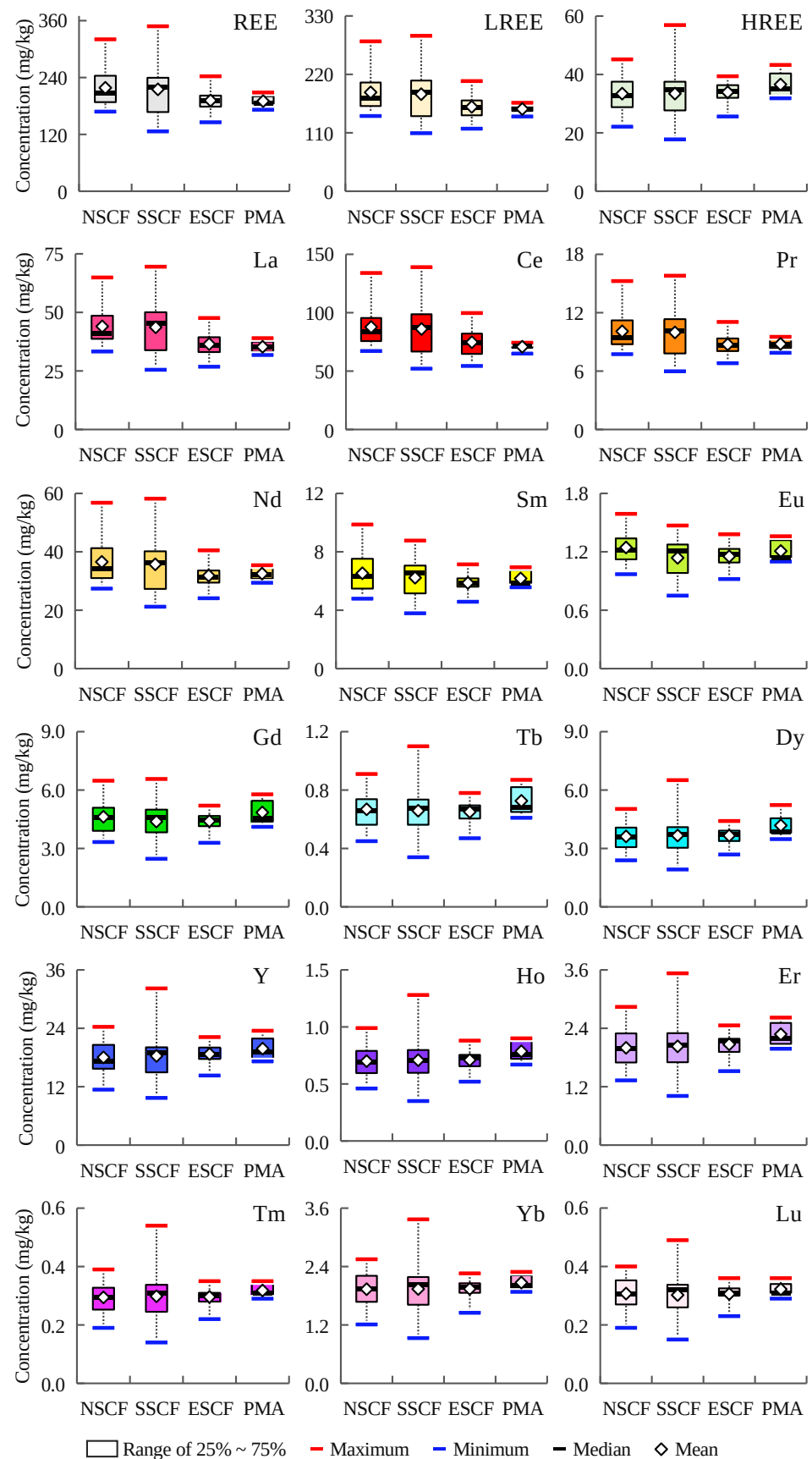


Figure 3. Concentrations (mg/kg) of REE in the soil of spontaneous combustion coalfields.

The mean concentration of NSCF was generally higher than the median (where Tm, Yb, and Lu were normally distributed), with a peak skewed to the right. Meanwhile, in SSCF, quite to the contrary, the distribution was left-skewed. The ESCF region had a right-skewed distribution for LREE (except Eu) and a left-skewed distribution for HREE (except Y). Right-skewed distributions were present in all but Ce in the mine PMA. All the LREEs (La, Ce, Pr, Nd, Sm, Eu) presented that the median concentrations in NSCF and SSCF were higher than ESCF and PMA. The concentration of each HREE in PMA was higher than in the coalfields. The concentration in SSCF had strong discreteness according to the quartile, and NSCF was second, whereas ESCF had high centrality and was close to PMA. Further, the coefficient of variation of the coalfields also provided evidence for this (Figure 4); apart from Sm, all elements have the highest coefficient of variation in SSCF, and all coefficients of variation in NSCF except Sm were below SSCF but higher than ESCF and PMA.

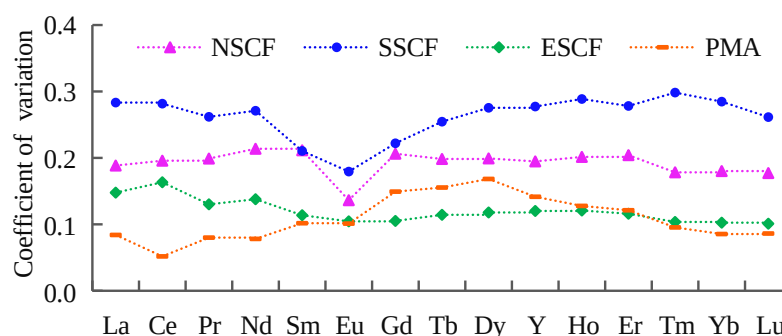


Figure 4. Coefficient of variation of REE in the soil of spontaneous combustion coalfields.

3.2. REE Concentration of the Soil Profiles

The changes in REEs in the soil profiles of each coal field were analyzed to further investigate the absorption and retention of REE by various substances in the soil (Figure 5). The plotted results indicated that Σ REE in NSCF showed the lowest value at 5 cm depth but presented a sharp increase at 20 cm and then gradually decreased over the segment of 20 to 60 cm and essentially leveled off below 60 cm. The graphs pertinent to Σ LREE showed a similar trend to Σ REE. However, the plots of Σ HREE exhibited a slight difference from them. The REE concentration in SSCF obtained valley values at a depth of 60 to 80 cm. Σ REE and Σ LREE separately decrease by -1.37 and -1.25 mg/kg/cm from 5 cm to 80 cm, and such a reduction is more apparent at a depth of 5 to 20 cm and 40 to 60 cm. The overall variation in Σ HREE was similar to that of Σ REE, but its concentration increased in the range of 5–20 cm. The REE concentration in the ESCF soil profile changed smoothly with increasing inclination from shallow to deep soil. With growing the soil depth, the concentrations of Σ REE, Σ LREE, and Σ HREE increased by 0.18, 0.13, and 0.05 mg/kg/cm, respectively, and the coefficient of variation was 0.05, 0.04, and 0.07, respectively.

A graphical representation of each REE was presented for more specific research. Among the LREEs, La, Ce, Pr, and Nd in coal fields all exhibited the same tendency as Σ LREE. Furthermore, all HREEs (i.e., Tb, Dy, Ho, Er, Tm, Yb, and Lu) except Ga and Y in NSCF, SSCF, and ESCF had the same sort order as the concentration in the depth range of 20–40 cm, while in the depth of 60 to 80 cm, their concentrations are extremely close.

In general, ignoring topsoil (i.e., 5 cm) strongly influenced by human activities and the external environment, the REE changes in NSCF and SSCF soil profiles, where the spontaneous combustion of coal occurs, were similar. Specifically, the concentration in the shallow layer was higher than that in the deep layer; however, in the ESCF, where coal combustion became extinct, the opposite trend was detected.

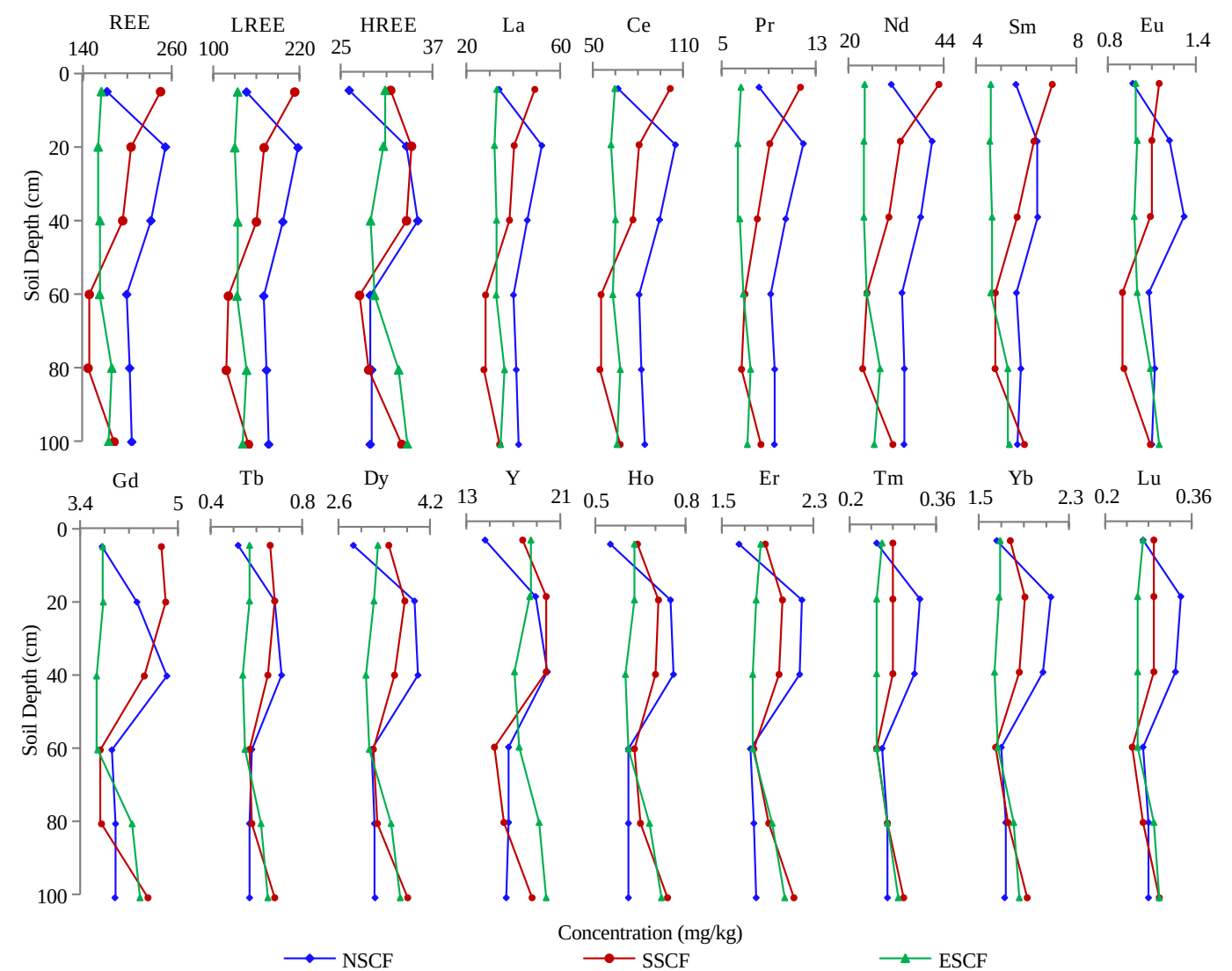


Figure 5. Variation curve of REE concentrations (mg/kg) in soil depth.

3.3. Distribution Patterns of Light and Heavy Rare Earth Elements

The distribution of REE follows the Oddo–Harkins’ law that elements with even atomic numbers are generally more abundant than adjacent elements with odd numbers in the Earth’s crust [36]. Therefore, the REE concentration in chondrites was considered as the reference value of REE in the soil to weaken the effect of even and odd and related phenomena and obtain the allocation of light and heavy REE in soil [37]. In 1984, Boynton gave a recommended value for the content of rare earth elements in chondrites by 22 chondrite samples (Table 1) [37].

Table 1. Concentrations of REEs in chondrites.

Elements	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	0.310	0.808	0.122	0.600	0.195	0.0735	0.259	0.047	0.322	0.0718	0.21	0.0324	0.209	0.0322

The chondrite standard curve of REEs in the soil of coal fields and PMA all showed a downward slope. The slope of La–Sm was higher than Gd–Lu (Figure 6), indicating that the REE has substantial differentiation, such as the systematic enrichment of LREE and depletion of HREE, especially in the NSCF and SSCF coal fields. The standard curves of

NSCF and SSCF were fitted to a very good degree, both slopes being higher than ESCF and PMA in the La–Sm span, confirming that LREE is richer in NSCF and SSCF. The ESCF chondrite standard curve approached PMA after several years of soil self-purification. The standard curve of chondrite of the La–Sm segment was low in PMA compared with the coal fields in MA, but the Gd–Lu segment exhibited a statistically higher value than the coal fields in MA.

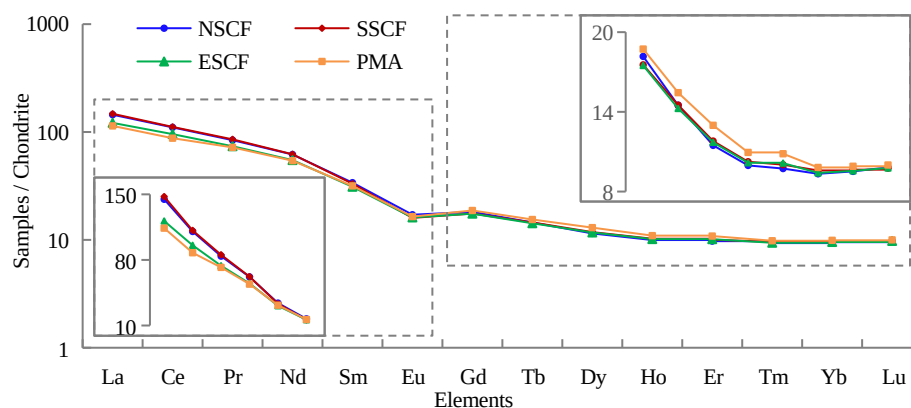


Figure 6. REE distribution patterns of various spontaneous combustion coalfields and PMA.

Moderately negative anomalies of Eu in NSCF, SSCF, ESCF, and PMA revealed that δEu values were below 0.67 (Table 1). Ce did not exhibit abnormality in the standard curve, and the values of δCe in NSCF, SSCF, ESCF, and PMA in order were 0.96, 0.95, 0.98, and 0.95. In addition, the value of $\delta\text{Ce}/\delta\text{Eu}$ varied between 1.45 and 1.52 in the studied area.

The $(\text{La}/\text{Lu})_{\text{N}}$ of soil in MA varied from 10.30 to 23.51 (Table 2), $(\text{La}/\text{Sm})_{\text{N}}$ is located in the interval of 3.37–5.88, and $(\text{Gd}/\text{Lu})_{\text{N}}$ ranged from 1.46 to 2.62. The REE enrichment pattern in this mine demonstrated the presence of LREEs. The values of $(\text{La}/\text{Lu})_{\text{N}}$, $(\text{La}/\text{Sm})_{\text{N}}$, and $(\text{Gd}/\text{Lu})_{\text{N}}$ in NSCF, SSCF, and ESCF indicated that the LREE enrichment degree in SSCF was higher than that in NSCF, which higher than ESCF. The values of $(\text{La}/\text{Lu})_{\text{N}}$ and $(\text{La}/\text{Sm})_{\text{N}}$ in PMA were lower than those of MA, while the value of $(\text{Gd}/\text{Lu})_{\text{N}}$ (i.e., 1.87) was slightly higher than MA (i.e., 1.82); further, the enrichment pattern was L-REE. Compared with MA, the LREE enrichment degree in PMA was lower, but HREE was slightly higher.

Table 2. Eigenvalues of REE from the soil in spontaneous combustion coalfield.

Region	δCe	δEu	$\delta\text{Ce}/\delta\text{Eu}$	$(\text{La}/\text{Lu})_{\text{N}}$	$(\text{La}/\text{Sm})_{\text{N}}$	$(\text{Gd}/\text{Lu})_{\text{N}}$
NSCF	0.96	0.67	1.46	14.75	4.30	1.84
SSCF	0.95	0.64	1.52	15.34	4.42	1.83
ESCF	0.98	0.66	1.47	12.46	3.91	1.79
MA-Mean	0.96	0.65	1.48	14.30	4.23	1.82
PMA	0.95	0.65	1.45	11.40	3.61	1.87

The standard curve of the soil profiles in NSCF, SSCF, and ESCF were consistent with their topsoil (Figure 7), demonstrating a tendency to be steep in La–Sm and steadily decreasing in Gd–Lu with moderate negative abnormalities of Eu and the LREE enrichment pattern of REEs. The values of δEu of the soil profile of NSCF, SSCF, and ESCF were obtained as 0.67, 0.62, and 0.71, respectively, and δCe was 0.97, 0.96, and 0.98. Compared to NSCF and SSCF, LREE differentiation in ESCF was relatively small, with the standard curve being similar among different soil depths due to the homogeneous textural composition of the soil from top to bottom layers.

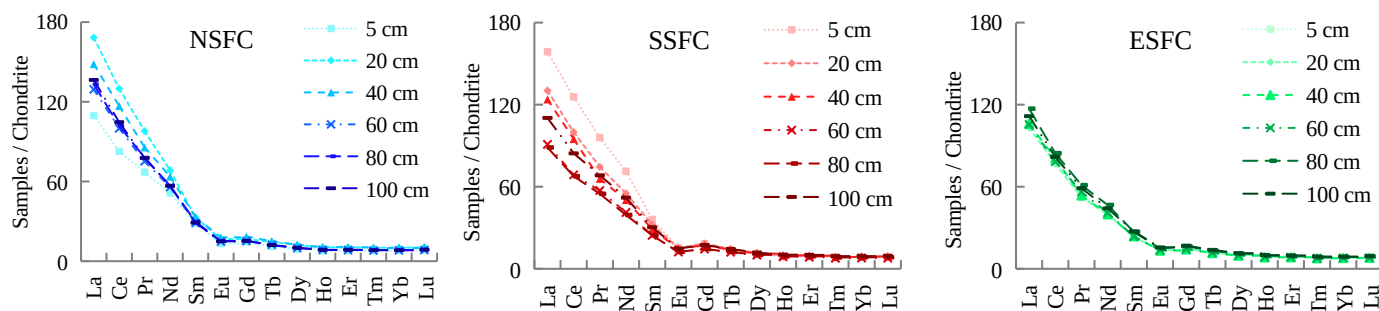


Figure 7. REE distribution patterns of soil profile in NSCF, SSFC, and ESFC.

3.4. Relationships between Common Elements and REE

A correlation analysis of the common elements with REE was utilized to confirm the mutual effects between REE and common elements (Figure 8). Both LREE and HREE were positively correlated with Aluminum (Al) and Titanium (Ti), both of which were significantly correlated with 99% confidence. Calcium (Ca), sodium (Na), and magnesium (Mg) showed a significant negative correlation with LREE, whereas ferrum (Fe), sulfur (S), and phosphorus (P) also exhibited a negative but not significant relationship. The relationship between Ca, Na, Mg, Fe, S, P, and HREE, different from LREE, was revealed in the significantly negative correlation of S and HREE, and Na was second (confidence). In addition, Fe, Mg, and P exhibited a weak positive correlation.

Each REE with common elements was charted for further investigation. Aluminum and Ti may have a positive effect on the enrichment of any REE, especially La, Ce, Pr, Nd, Sm, Tm, Yb, and Lu, which all reached confidence in the range of 95% to 99%. In addition, Ti also played a positive role in the enrichment of Tb, Dy, and Ho. Calcium and Na probably caused the loss of La, Ce, Pr, Nd, and Sm, but they both had weak effects on all HREEs. Magnesium can also deplete La, Ce, Pr, and Nd but can partially accumulate Dy, Ho, and Er. Sulfur was negatively correlated with all elements, of which Dy, Y, Ho, Er, Tm, Yb, and Lu reached a level of confidence of 99% and Tb reached a level of confidence of 95%. With the increase in relative atomic mass from Gd to Lu (except Y), the correlation with S is remarkably enhanced. Phosphorus may contribute to the enrichment of Dy, but it could deplete the content of La and Ce. Ferrum exhibited a weak effect on REE, with only Eu showing a positive correlation of 95% confidence.

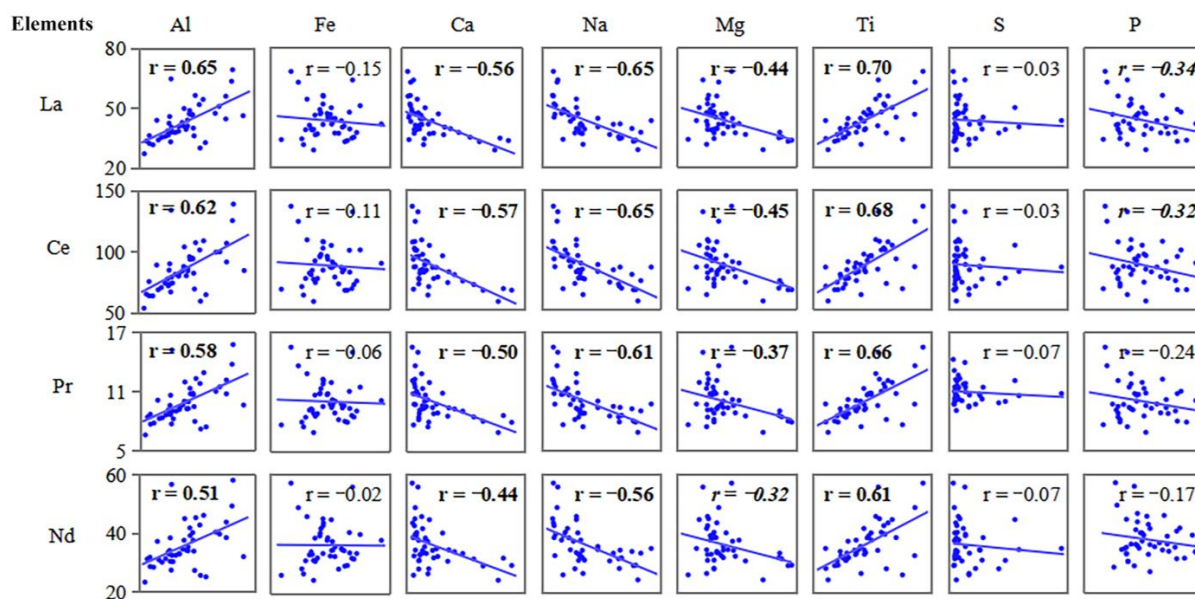


Figure 8. Cont.

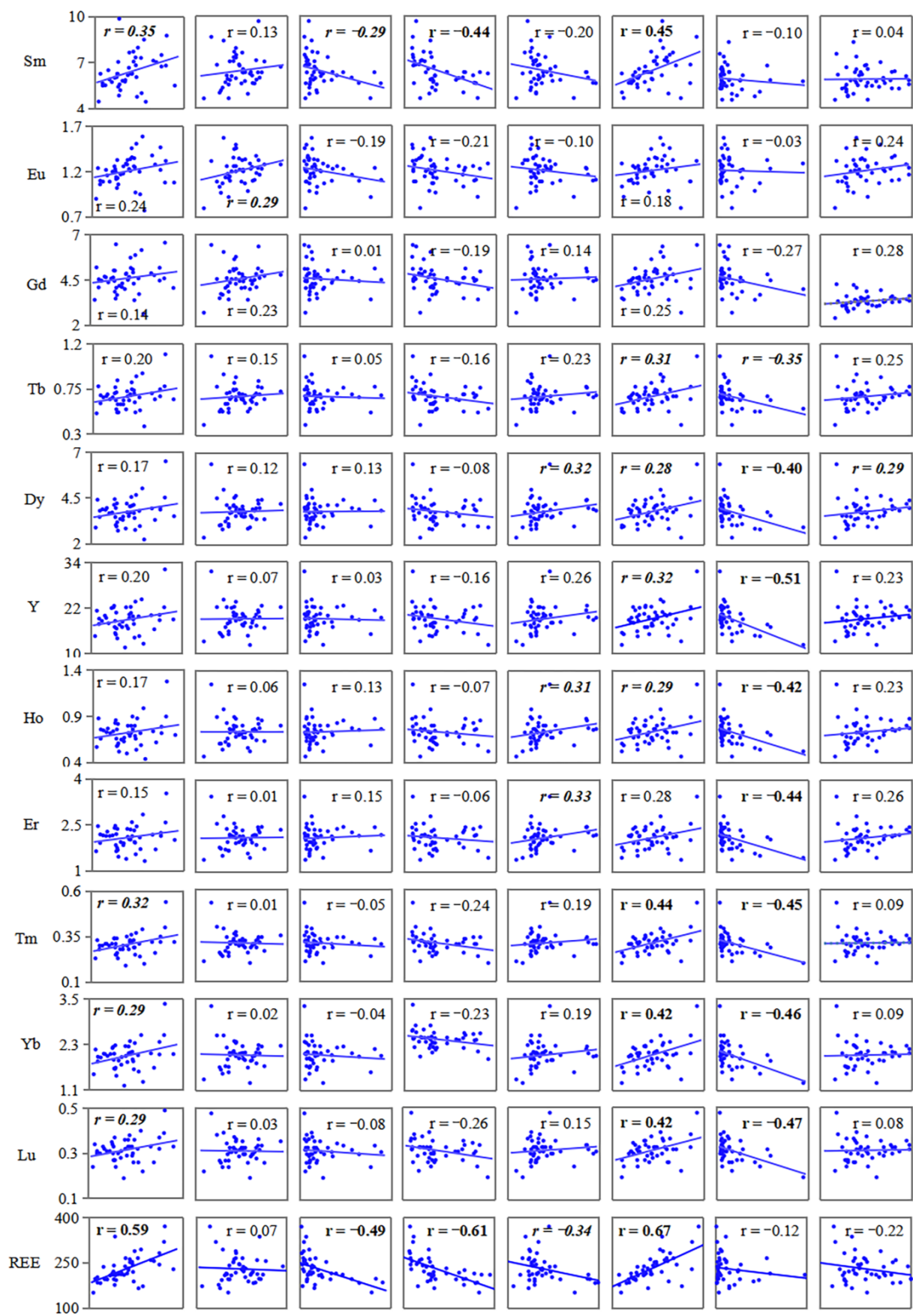


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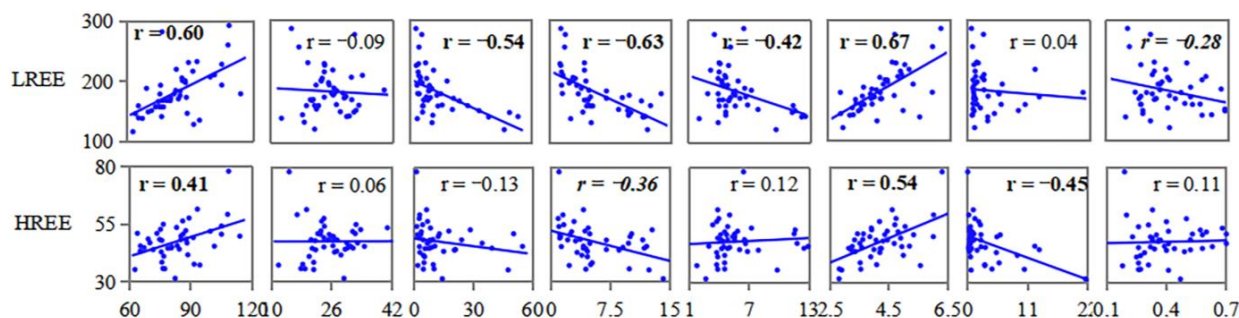


Figure 8. Correlation analysis of the most common elements and REE.

Overall speaking, the effects of common elements on light and heavy REEs are significantly different from each other. Aluminum and Ti had a similar effect on REE, which may have the same source of materials and the same geochemical behavior. The effects of Fe and P on REE were almost unclear. Further, S can cause a deficit of all REEs, especially for the heavy elements. Calcium, Na, and Mg could decrease LREE but exhibited a different effect on HREE.

4. Discussion

4.1. REE Differences among Each Coalfield

The REE concentration in the soil of the Rujigou mining area was higher than the average value of Chinese surface soil (180 mg/kg), upper crust (169 mg/kg) [38,39], and coal (136 mg/kg) [40], and even several times higher than the world average for coal (i.e., 68.47 mg/kg) [41]. However, even up to 403.5 mg/kg global mean REE in coal ash [42], REEs in lignite (378 mg/kg) and bitumite (469 mg/kg) ash were 5.48 and 6.51 times that found in the coal itself (69 and 72 mg/kg, respectively), and REEs in the bottom band bituminous coal ash in central and eastern Kentucky were as high as 1965–4198 mg/kg [42]. In general, the REE concentration of coal ash is substantially higher than that of coal itself [43], so the coal combustion process can increase the REE enrichment to some extent [44,45].

The main reason for the REE differences among each coalfield is that the SSCF was affected by sustained coal combustion during the 30-year observation period (i.e., the coal in this field had a high combustion intensity and high slag ratio). On one hand, particulate matter like coal ash can be dispersed into the atmosphere with smoke from coal combustion, scatter to the soil surface as a result of dust fall, and finally penetrate the soil through surface runoff infiltration processes. On the other hand, water molecules produced by underground coal seam combustion can also retain REEs in soil. NSCF was also affected by coal spontaneous combustion, but the Σ REE was lower than SSCF due to the shorter spontaneous combustion period. Spontaneous combustion also occurred in the ESCF, but after the coal fire was extinguished, soil self-purification and the leaching of soil water seepage carried REEs from the surface and shallow soil to the deeper layer, which reduced the REE concentration in the soil compared with the combustion stage.

To further validate the effects of coal spontaneous combustion on REEs, the concentration of REEs in the raw gangue and the burned gangue were compared and analyzed (Table 3). In general, the Σ LREE of the burned gangue (126.16 mg/kg) was higher than the raw (37.97 mg/kg), with a difference value of 88.19 mg/kg, while the Σ HREE of the burned gangue (18.93 mg/kg) was lower than the raw (23.51 mg/kg) with a difference value of 4.58 mg/kg. Interestingly, the multiples of LREE concentrations experienced a downward trend, with values of 4.92, 3.70, 3.23, 2.40, 1.15, and 0.73, of which only Eu reached a lower concentration in the burned gangue compared with the raw; this may be caused by the chemical activity of elements, such that the reactivity of La, Ce, Pr, Nd, Sm, and Eu ranks in descending order. For the multiples of HREEs, concentrations appeared to increase severely with an opposite tendency, of which Gd, Tb, Dy, Ho, Er, Tm, and Yb

progressively increased with the values of 0.70, 0.74, 0.79, 0.84, 0.99, 1.27, and 1.40. Lu and Y, in order, reached 1.36 and 0.77.

Table 3. Concentrations of REEs in the gangue and their multiples.

Elements	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
Raw	6.4	16.6	2.09	9.5	2.93	0.45	3.07	0.43	2.42	14.8	0.45	1.18	0.15	0.87	0.14
Burned	31.5	61.4	6.75	22.8	3.38	0.33	2.16	0.32	1.90	11.4	0.38	1.17	0.19	1.22	0.19
Multiple	4.92	3.70	3.23	2.40	1.15	0.73	0.70	0.74	0.79	0.77	0.84	0.99	1.27	1.40	1.36

4.2. REE Differences in Soil Profiles

The upper layer in the NSCF was the soil with smaller particle diameters, while the layer below 60 cm was bedrock debris. There are many and varied existing forms of REE in soils, such as organic combination, inorganic combination, iron–manganese oxides, one of which is easy to be adsorbed by clay minerals, and Al, Ca, K, Mg, and other elements as the main components of clay minerals [46]. Therefore, the Σ REE in the upper layer was higher than in the lower layer. In addition, mountain collapse caused by coal fires in the northeast of this soil profile may cause the plastic deformation of the underlying rock layers and change the basic structure of the soil layer, resulting in substantial differences in the REE concentration of upper and lower soil layers.

The rock layers in the coal mining area can be divided into a caving area, a fracturing area, and a sinking area in the vertical direction. Due to the uneven surface subsidence, tensile deformation gradually appeared at the edge of the surface subsidence basin and the boundary of the goaf and finally led to the formation of surface cracks. The fracturing and movement of overlying layers in a coalfield after combustion exhibit similar characteristics to the coal layers in which it was mined. Profile samples in SSCF were obtained in the fracture caused by coal combustion and acted as a channel for the oxygen supply in the combustion fields and smoke escape from the burned underground coal seams. Some of the chemical elements in the soot were dispersed into the atmosphere by the airflow over the surface, and some were trapped above the cracks at the angles between the crack and the ground plane due to the change in the airflow field. As a result, Σ REE in this profile gradually increased from the bottom to the top.

The thickness of the ESCF soil layer was large, and the soil texture was relatively uniform from top to bottom, so Σ REE changed continuously with increasing soil depth.

On the whole, REE concentration in the upper soil layer of the combustion fields in the Rujigou mine was higher than the deeper surface, except for the topsoil (i.e., a surface layer thickness of 5 cm). One of the main factors is that the topsoil is resistant to extreme weathering and is more easily eroded by water and wind erosion, which makes it easier for elements to be lost. On the other hand, mine plants are mainly herbaceous and have shallow root systems that may absorb and enrich elements in topsoil. In addition, the infiltration of surface water brings the surface soil REEs to the deeper layer; therefore, the REE concentration in the depth range of 20–40 cm was relatively higher.

4.3. REE Distribution Patterns

The REE fractionation could reflect the material source and evolution of the soil depositional environment [36]. According to the value of $(\text{La}/\text{Lu})_{\text{N}}$, $(\text{La}/\text{Sm})_{\text{N}}$, and $(\text{Gd}/\text{Lu})_{\text{N}}$, Seredin and Dai [47] classified the enrichment patterns of REE into L-REE ($(\text{La}/\text{Lu})_{\text{N}} > 1$), M-REE ($(\text{La}/\text{Sm})_{\text{N}} < 1$ and $(\text{Gd}/\text{Lu})_{\text{N}} > 1$), and L-REE ($(\text{La}/\text{Lu})_{\text{N}} < 1$).

REEs typically exist as trivalent cations in carbonates, phosphates, silicates, and oxides [28]. Ce^{3+} is easily oxidized to Ce^{4+} and hydrolyzed to precipitate $\text{Ce}(\text{OH})_4$ or absorbed by hydroxide, manganese oxide, and ferric oxide with changes in the humidity and acidity of the environment. Therefore, oxidizing conditions are suitable for Ce enrichment, and Ce anomalies always reflect the soil REDOX environment [48–50]. The leaching of Eu^{3+} deep in the soil in the reducing environment and the further loss of Eu^{2+} in the reduction

process ultimately causes europium anomalies. In addition, volcanic hydrothermal fluid, basic rock, and calcium-rich minerals may result in positive Eu anomalies [51–53]. δEu and δCe are often exploited to indicate the abnormality of Eu and Ce. When its value is less than 1, the anomaly is negative; otherwise, it is positive. When the value of $\delta\text{Ce}/\delta\text{Eu}$ is greater than 1, the coal formation conditions are dominated by the reducing environment, and conversely, by the oxidizing condition [54,55].

Moderate negative Eu anomalies in the studied area imply that the primary source of REE in this area was weathering, transport, and the deposition of acidic, intermediate rocks or some soil-forming debris [56]. Cerium showed no abnormality in the normalized curve, indicating that the soil in this region was formed under weak reduction. The mineral elements in soil parent materials are primarily controlled by the reducing environment, as indicated by the $\delta\text{Ce}/\delta\text{Eu}$ in MA and PMA.

4.4. Impact Factors of REE

Characterizing the influencing factors of REE would allow us to analyze the environmental evolution of mine soil during the weathering and soil formation process, leading to the exploitation and utilization of rare earth resources. The exploitable rare earth minerals mainly include monazite ((Ce, La) PO_4), bastnaesite (Ce, La) $[\text{CO}_3]\text{F}$, allanite $(\text{Ca,Ce})_2(\text{Fe}^{3+},\text{Fe}^{2+})(\text{Al},\text{Fe}^{3+})_2[\text{Si}_2\text{O}_7][\text{SiO}_4]\text{O}(\text{OH})$, and xenotime ($\text{Y}[\text{PO}_4]$) [28,57]. Apart from that, REEs are much more easily adsorbed in inorganic minerals like SiO_2 , Fe_2O_3 , Al_2O_3 , MgO , and CaO or combined with organic matter [40], and the common elements such as Al, Ca, Mg, Na, and Fe are the essential ingredient of clay minerals [58].

Research has shown that REE is closely related to common elements, but common elements have different effects on REE. In the Rujigou Mine, Al and Ti in soil may contribute to REE enrichment. These results are consistent with soil studies in Xinmi coal [58] and basalt weathering on the Boloven Plateau [59]. Calcium, Na, and Mg in Rujigou mine soil could decrease LREE, while in Xinmi coal, ΣREE was positively correlated with Na and Mg with correlation coefficients of 0.82 and 0.72, respectively. Yang et al. [58] displayed that the REE concentration in the red soil of southern China was positively correlated with Fe_2O_3 , while according to Zhang et al. [60], ΣREE in basalt-derived soil in the Leizhou Peninsula showed a significant negative correlation with Fe_2O_3 , which may be attributed to the increased crystallization of iron oxides and decreased REE-rich amorphous iron concentration. The effect of P on the REEs at Rujigou was negligible, but in basalt weathering on the Boloven Plateau, REEs were enriched in samples rich in P_2O_5 [59]. Sulfur in Rujigou mine soil can cause the deficiency of REEs, especially heavy elements. This negative correlation was more significant with the increase in relative atomic mass from Gd to Lu. This phenomenon may be influenced by the bisulfate dissociation constant (HSO_4^-) converted from sulfur molecules after combustion [61].

5. Conclusions

- (1) The REE concentration in the soil of the Rujigou Coal Mine was about 216.09 mg/kg, of which LREE is 84.55%. The sum of REEs and LREEs were lower in PMA than MA, but ΣHREE is higher. The sum of REE in SSCF was similar to NSCF and higher than ESCF. Coal combustion can contribute to LREE enrichment to some extent, while HREE may be depleted in the process.
- (2) The presence of ground cracks in the spontaneous combustion zone not only acts as a smoke evacuation channel but also disturbs the uniform distribution of REE. The vertical distribution of REE varies slowly in bedrock debris and soils with a uniform texture.
- (3) There was an apparent differentiation of REE in the mine that resulted in LREE enrichment and HREE deficiency, especially in the coalfield. All coalfields showed an LREE distribution pattern with a moderately negative Eu anomaly (δEu ranged from 0.64 to 0.67) and no significant Ce anomaly (δCe ranged from 0.95 to 0.98). The source

of REE material in this area may come from soil-forming clastic rocks such as acid or neutral rock, which are weakly controlled by reduction.

- (4) Aluminum and Ti might have the same material source as REEs, especially LREEs, because they have similar geochemical behavior. Sulfur and Fe had a negligible relation with the enrichment and distribution of REEs, while Ca, Na, and Mg had a negative correlation with LREEs.

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