RARE EARTH ELEMENTS DISTRIBUTION CHARACTERISTICS OF *LARIX GMELINII* FOREST SOILS IN NORTHERN DAXING'ANLING MOUNTAINS

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Abstract. Rare earth elements (REEs) have unique geochemical habits and have been widely recognized and applied in many aspects of the environment as a geochemical indicator. They are widely used in the homology determination study of different geological bodies. However, there is limited information on the distribution patterns and influencing factors of REEs in cold temperate forest soils. The *Larix gmelinii* is a dominant tree species in the cold temperate zone. This study aims to study the characteristics of REEs of three *Larix gmelinii* forest soils in northern Daxing'anling Mountains. A total of 112 representative soil samples were collected and the concentrations of 14 REEs were determined using X-ray fluorescence. The results show that: (1) The order of REEs content in *Larix gmelinii* soil is: Ce > La > Y > Gd > Dy > Yb > Sm > Er > Pr > Eu > Ho > Tb > Tm > Lu, which follows the Oddo-Harkins rule. The mean content of REEs in the *Larix gmelinii* soil is lower than the national and global average; the soil environment is basically safe under human disturbance. (2) The total REEs show an increasing trend with the depth of the soil profile, and tends to be gradual after 20 cm. The content of REEs in the three types of forest soils is in the order of Grass-*Larix gmelinii* forest (GL) > Ledum-*Larix gmelinii* (LL) > *Rhododendron-Larix gmelinii* (RL). (3) The relationship between REEs indicators and pH is significant, with ∑REE, LREE, HREE, LREE/HREE and pH showing a significant positive correlation, δEu, δCe and pH showing a significant negative. Understanding the distribution, migration, and transformation patterns of REEs in forest soil can help reveal the cycling mechanism of elements in forest ecosystems, provide guidance for improving forest soil fertility and promoting plant growth, and provide a basis for monitoring and evaluating the impact of human activities on forest soil environment.
Keywords: *rare earth elements, profile characteristics, forest types, cold temperate, differentiation patterns*

Introduction

Rare earth elements (REEs) are the general name of 17 metal elements in the chemical periodic table including lanthanide elements, scandium, and yttrium. According to the atomic electron layer structure and physicochemical properties, as well as characteristics of their coexistence in minerals and varied properties resulted from different ionic radii, these REEs are usually divided into two groups: light rare earth elements (LREEs), including La, Ce, Pr, Nd, Pm, Sm, Eu; heavy rare earth elements (HREEs), including Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y.

The stock of REEs in plants is relatively small, and they often coexist together in natural environments with similar atomic structures and ionic radii. Due to the special physical and chemical properties of REEs, they have been widely used in industries such as metallurgy, fluorescent materials, dyes, glass ceramics, hydrogen storage materials, petrochemicals, biopharmaceuticals, and polymer materials (Zhong, 2012).

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With the widespread development and application of REEs, a large amount of REEs elements have entered the environment (Wang and Liang, 2016; Silva et al., 2018), and the biological and environmental effects of REEs have become important research topics (Miao et al., 2007). However, to know the natural level of REEs in soils is the first step in monitoring potentially contaminated area (Silva et al., 2018).

In recent years, REEs have also been widely applied in agriculture. They are usually used as trace elements in fertilizers, can improve soil properties; and also, can enhance the plant's stress tolerance and nutrient uptake. More and more studies have found that REEs can improve plant photosynthetic efficiency, promote seed germination and root growth, improve stress resistance and disease resistance of plants, thus effectively improve crop yield and quality (Hu et al., 2004; Tang et al., 2016; Wang et al., 2016; Zhang et al., 2023). In general, the content and distribution characteristics of REEs in soil depend not only on the composition of bedrock and soil parent material, but also closely related to soil formation process, soil type, soil physicochemical properties, water dynamics, natural environmental characteristics, and human activities (Chen et al., 2011).

China has the largest reserves of RE resources in the world. Chinese scholars have studied the geochemical characteristics of REEs in different regions and plants (Wang et al., 2014; Zhang et al., 2019; Zhang et al., 2023): (1) Researches on the geochemical characteristics of REEs in surface soils of different regions are mostly focused on southern regions of China, such as Guizhou, Jiangxi, Hainan, Huzhou, and western Guangdong. However, there are relatively few reports on rare earth elements in soil in Northeast China, especially in cold temperate regions. (2) Researches on geochemical characteristics of REEs in different mining areas were conducted, such as Anshan Iron Mine, Dabaoshan Polymetallic Mine and Lead-Zinc Deposit in Northwest Guizhou. (3) Geochemical characteristics of REEs in economic crop producing areas, such as *Lycium bararum* (Qi et al., 2014), navel orange orchard (Zhong, 2012), and Tea (Bian et al., 2017). Studies have shown that REEs can increase tea yield and improve tea quality in a certain concentration range, but exceeding the critical content can be inhibited or even toxic (Pagano et al., 2015; Bian et al., 2017). Researches have shown that some trace elements and REEs are not easily fractionated during chemical weathering and migration, and can serve as good indicators for the source and sedimentation process of aeolian sediments (Zhang et al.,2018). Scholars have studied the migration and transformation characteristics of REEs in soil-plant system, the results show that no big difference was found within a soil-plant system in REEs distribution pattern, and REEs are obviously fractionated when they are transported and migrated from soils to plants (Miao et al., 2007). Up to now, there is little information about the REEs characteristics in natural forest soils, especially in cold temperate regions.

As an important part of the northern forest belt of Eurasian continent, the forest region of Daxing'anling Mountains has a complete natural ecosystem of forest, grassland, and wetland. It has special ecological protection functions and multiple associated resources and is a national key carbon storage base. It is known as the "Green Great Wall" and "Important Ecological Barrier" of Northern China. The Daxing'anling forest area is located in a high latitude and cold zone. Where the soil layer is barren and the tree growth is slow. Once destroyed, it cannot be replicated. The accumulation of REEs in the soil has become an environmental concern. In this context, we aim to determine the natural levels of REEs in soils under cold-temperate climate conditions, to analyze the differences in soil REEs characteristics among different forest

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types, and to evaluate the influence of soil pH on the geochemistry of REEs. This study fills a gap in the scarce data on surface geochemistry of REEs in Daxing'an Mountain.

Materials and methods

Study area

The study area (50 49'-50 51'N, 121 30'-121 31'E) is located in Chaocha Forest Farm of Genhe Forestry Bureau, Inner Mongolia, China, where the forest coverage is 75%. The altitude varies from 810 m to 1100 m in this area. It belongs to the cold temperate and semi-humid climate zone with a freezing period of 6-7 months. The annual average temperature is - 5.4℃, and the minimum temperature is - 50℃. Most of the rainfall is concentrated from July to August, with annual precipitation of 438-530 mm. The main soil type in this area is brown coniferous forest soil. There are large areas of permafrost distributed for many years. *Larix gmelinii* is the dominant tree species. Due to the differences in site conditions and altitude, the main forest types are *Rhododendron-Larix gmelinii* forest (RL), Ledum-*Larix gmelinii* forest (LL), and Grass-*Larix gmelinii* forest (GL). The main undergrowth plants are *Rhododendron dahuricum*, *Ledum palustre*, *Vaccinium vitis-idaea*, and *Pyrola incarnata*.

Sample collection and determination

A total of 28 sample plots (30 m × 30 m) of different forest types of *Larix gmelinii* forest (RL, LL, GL) were set up. In each sample plot, three soil samples were laid out by diagonal plot method. Soil samples were collected in the sealed bags using a stainless-steel shovel according to 0-10 cm, 10-20 cm, 20-40 cm, and 40-60 cm. Physical and chemical properties of soil samples were analyzed in laboratory.

A total of 112 soil samples were dried naturally and sealed after sorting and crushing and through 2-mm sieve. The contents of REEs were determined by X-ray fluorescence spectrometer (BRUKER S8 TIGER SERIES 2, Germany) including 14 elements (La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). Soil pH was measured using a pH meter with a soil/water mass ratio of 1:5 (w/v).

Data statistics

LREE/HREE was used to express fractionation between LREEs and HREEs. The large ratio shows there are obvious fractionation between LREEs and HREEs, the larger values indicate that the LREEs are relatively enriched and the HREEs are relatively deficient. Internal fractionations of LREE and HREE were quantified by $(La/Sm)_N$ and $(Gd/Yb)_N$, respectively. Specifically, Eu and Ce anomalies δCe and δEu were calculated according to Compton et al. (2003) as *Equations 1* and *2*, values over 1 indicate enrichment relative to UCC.

$$\delta Eu = Eu / Eu^* = Eu_N / (Sm_N \cdot Gd_N)^{1/2} \quad \text{(Eq.1)}$$

$$\delta Ce = Ce / Ce^* = Ce_N / (La_N \cdot \mathrm{Pr}_N)^{1/2} \quad \text{(Eq.2)}$$

where Eu_N, Sm_N, Gd_N, Ce_N, La_N, and Pr_N are the standardized values of chondrite for the measured values of this element, respectively.

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Fractionations on the LREEs and HREEs $(La/Sm)_N$ and $(Gd/Yb)_N$ $(La/Yb)_N$ were quantified. The chemical alteration index (CIA) was calculated following the methodology of Nesbitt and Young (1982) as *Equation 3:*

$$CIA = [Al_2O_3 / (Al_2O_3 + Na_2O + CaO + K_2O)] \times 100 \qquad \text{(Eq.3)}$$

where Al_2O_3, Na_2O, CaO, and K_2O refer to their molar fractions.

Correlation analysis between various indicators were investigated using Pearson Correlation Analysis. SPSS 21, Origin 2019, and excel 2016 were used for statistical analysis and mapping of data.

Results

REEs concentrations in soil

Basic statistical characteristics on REEs

The statistical values of REEs can be seen in *Table 1*. The ∑REE in soil ranged from 75.61 mg/kg to 136.62 mg/kg, with mean of 102.04 mg/kg, standard deviation of 14.41 and variation coefficient of 0.14. The LREE content ranged from 47.51 mg/kg to 96.07 mg/kg, with mean of 67.45 mg/kg, standard deviation of 11.96 and variation coefficient of 0.18, indicating that the LREE distribution was uneven. HREE content ranged from 28.10 mg/kg to 40.74 mg/kg, with mean of 34.59 mg/kg, standard deviation of 3.22 and variation coefficient of 0.09. Except Pr and Sm, the variation coefficient of each element content is less than 0.2, which indicates that the variability of element content is low and the soil environment is basically safe under the disturbance of human factors.

The average content of REEs in the surface soil of the study area follows the Oddo-Haggins rule, that is, the content of even atomic number of REEs is higher than that of odd atomic number of adjacent two elements, and the average content of LREEs is higher than that of HREEs.

Differentiation patterns on REEs

The LREE/HREE is the ratio of LREEs and HREEs, which reflects the fractionation degree between LREEs and HREEs in samples to a certain extent. The LREE/HREE ranges from 1.56 to 2.46, with an average value of 1.95, which is larger than 1. This indicates there are certain differences between LREEs and HREEs in the soil of the study area, and that LREEs are relatively enriched. However, the value is significantly lower than the national mean value, indicating that the advantages of LREEs in the total amount of RE are not obvious, and the enrichment characteristics of LREEs are not significant. The $(La/Sm)_N$ ratio and $(Gd/Yb)_N$ ratio changes in a small range, indicating that the internal fractionation of LREEs and HREEs is weak.

Anomaly characteristics of Ce and Eu

The δEu and δCe values reflect the anomalies of Ce and Eu during the process of soil development, which are the important parameters reflecting the environment. δEu or δCe > 1.05, indicate positive anomalies; and δEu or δCe < 0.95, indicate negative anomalies (Wang et al., 1989). In this study, the δEu values ranged from 0.61 to 1.36

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with the mean value 0.95, close to 1, which indicate no anomaly for Eu in general. The δCe values ranged from 0.89 to 2.80 with mean value 1.39, which shows positive anomalies and relatively enriched Ce.

***Table 1.** Main parameters for REEs in surface soils*

REEs	Maximum (mg/kg)	Minimum (mg/kg)	Mean (mg/kg)	Standard deviation (Std., mg/kg)	Variation coefficient (C.V.)
La	29.51	17.45	22.72	3.18	0.14
Ce	55.23	26.58	38.27	6.95	0.18
Pr	6.62	0.38	2.50	1.60	0.64
Sm	4.33	1.78	2.87	0.66	0.23
Eu	1.43	0.81	1.09	0.18	0.17
Gd	6.00	3.36	4.53	0.73	0.16
Tb	0.92	0.46	0.63	0.12	0.19
Dy	4.86	2.32	3.20	0.63	0.20
Ho	1.03	0.69	0.84	0.09	0.11
Er	3.44	2.18	2.78	0.36	0.13
Tm	0.52	0.30	0.43	0.06	0.15
Yb	4.02	1.89	3.09	0.48	0.16
Lu	0.51	0.33	0.40	0.05	0.12
Y	24.34	13.66	18.69	2.56	0.14
∑REE	136.62	75.61	102.04	14.41	0.14
LREE	96.07	47.51	67.45	11.96	0.18
HREE	40.74	28.10	34.59	3.22	0.09
Indicators	**Maximum**	**Minimum**	**Mean**	**Standard deviation (Std.)**	**Variation coefficient (C.V.)**
LREE/HREE	2.46	1.56	1.95	0.24	0.13
δEu	1.36	0.61	0.95	0.19	0.20
δCe	2.80	0.89	1.39	0.44	0.31
La/SmN	7.26	4.00	5.11	0.86	0.17
Gd/LuN	1.85	0.93	1.40	0.25	0.17
Gd/YbN	1.70	0.84	1.21	0.29	0.24

Normalized patterns of REEs

The normalized patterns of REEs in soil can be used for provenance judgment and environment restoration. The research is not to use REEs' absolute content directly, but to standardize the measured data for chondrites. That is to say, dividing the measured content of each rare earth element by the corresponding element content of chondrites. After standardization of REEs, the sawtooth phenomenon of REEs abundance increasing with atomic number ("one high one low") can be eliminated. So any separation among REEs in the sample can be clearly shown. The mean value of chondrites proposed by Boynton (Han and Ma, 2003) was used to standardize the data measured in this study. After standardization, the chondrite-normalized REEs pattern can be obtained, as shown in *Figure 1*.

After chondrite standardization, the curve presents a distribution pattern with a negative slope. The section of La-Sm is steeper, while the section of Eu-Lu is gentle,

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which reflects the LREEs accounting for a large proportion of total REEs, namely, LREEs are more enriched. It shows the typical characteristics of REEs in the continental crust, which indicates the main material source is continent. Accumulation.

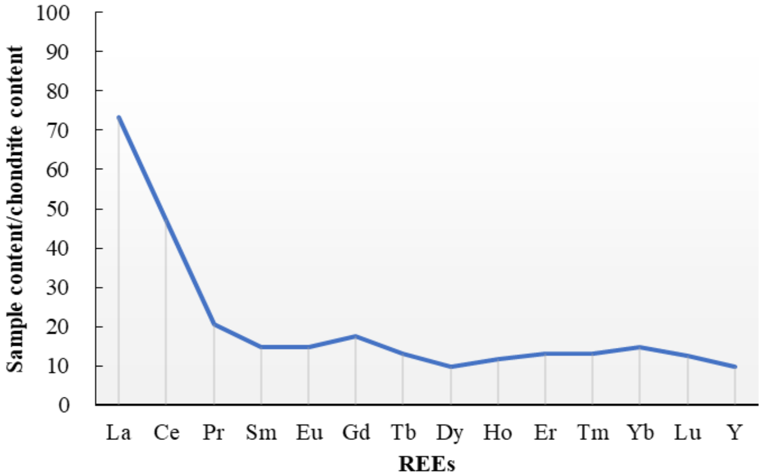

Figure 1. *Chondrite-normalized REEs distribution patterns of surface soils*

Profile characteristics of REEs

It can be seen from *Figure 2* that the total amount of REEs in the soil profile increases with the soil depth. The changes are obvious above 20 cm, and tends to be gentle below 20 cm with slightly decreasing at 40-60 cm. The mean LREEs and HREEs contents follow the similar rule. The distribution rule of LREEs is completely consistent with that of total REEs. It indicates LREEs is the main component of REEs and its change has great influence on the change of REEs to certain extent. While HREEs has been increasing from 0 to 60 cm. At the same time, it can be seen from the table that the value of LREE/HREE is 1.6-2.1(>1), which indicates there is certain fractionation between LREEs and HREEs.

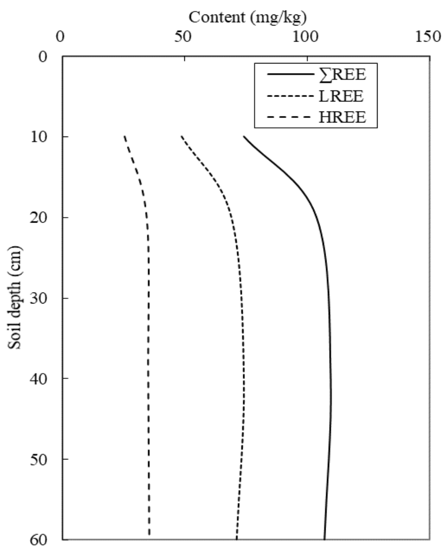

Figure 2. *Vertical distribution characteristics of REEs*

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The distribution curves of REEs in different soil depths after chondrite standardization are shown in *Figure 3*. The slope of the distribution curve from La to Eu increases gradually, and variations are smaller after Gd. Eu has slight loss at each soil layers relating to the loss of Eu^{3+} after leaching reduction. The differences between 0-10 cm soil layer and other layers is obvious with the content before Eu is lower than other layers. The content of Ce in the top layer (0-10 cm) is higher than that in the lower layers (10-20 cm, 20-40 cm and 40-60 cm).

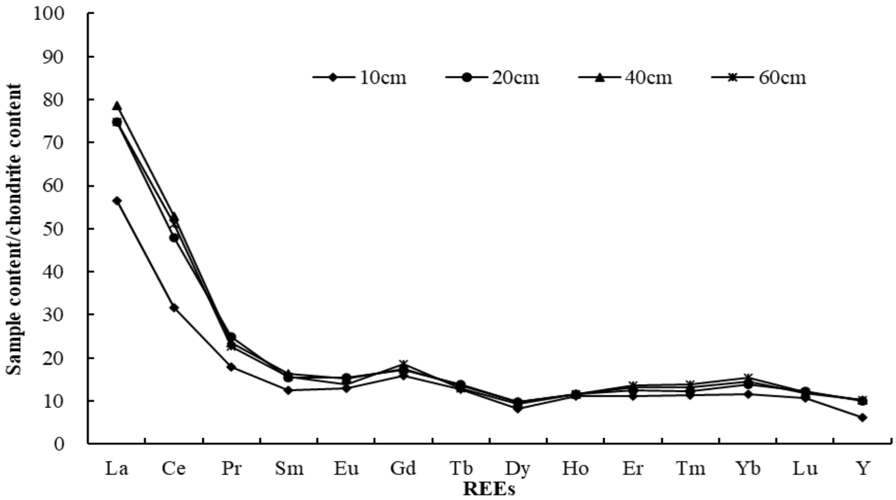

Figure 3. *Distribution patterns of REEs in soil profile*

The values of δ Ce and δ Eu at different depths are shown in *Table 2*. The mean value of δCe is 1.29-1.39 which is higher than that in the whole country (the average value of δCe in China is 0.976), and higher than that in the world (the value of δCe in the world is 0.719). The δCe values of each layer are larger than 1.05, showing obvious positive anomaly, which can be clearly observed from the distribution curve of each layer (*Fig. 4*). It also can be seen that δCe values are in order of bottom layer (40-60 cm) > middle layer (10-20 cm, 20-40 cm) > top layer (0-10 cm). The mean value of δEu is between 0.83 and 0.98, close to 0.95, which reflects Eu deficit not obvious in study area.

Table 2. *Statistical values of REEs indicators at different soil depths*

Depth (cm)	∑REE (mg/kg)	LREE (mg/kg)	HREE (mg/kg)	LREE/HREE	δEu	δCe
10	73.98	48.65	25.34	1.91	0.95	1.29
20	103.55	69.06	34.49	1.99	0.98	1.35
40	109.35	74.21	35.14	2.10	0.93	1.31
60	106.82	71.23	35.59	2.00	0.83	1.39

Distribution characteristics of REEs under different forest types

The ∑REE of three forest types (GL, LL, and RL) ranged from 98.82-136.62, 85.44-128.87 and 75.61-105.26 mg/kg, with mean values of 107.36, 102.10 and 92.60 mg/kg,

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respectively (*Table 3*). The coefficient of variation was close ranging from 0.13-0.14. The mean LREE was 72.12, 67.14 and 59.91 mg/kg, and the mean HREE was 35.24, 34.96 and 32.69 mg/kg, respectively. In terms of statistical indicators, the ∑REE is in order of GL > LL > RL, and the differences on LREEs were larger than that of HREEs (*Table 4; Fig. 4*). The LREE/HREE ratios of three forest types were 2.05, 1.91 and 1.83, respectively, which were all greater than 1. It indicated there is obvious fractionation between the LREEs and HREEs in three forest types, and the LREEs was relatively enriched. The δEu values of three forest types were 0.86, 0.98 and 1.01, respectively, which were slightly less than 1.05, showing negative anomalies and Eu deficit, especially in GL forest. The δCe values of three forest types were 1.24, 1.31 and 1.83, respectively, which were slightly higher than 1.05, showing a positive anomaly and Ce enriched, especially in RL forest (*Table 4*).

Table 3. *Statistical values of ∑REE under different forest types*

∑REE statistics	GL	LL	RL
Maximum (mg/kg)	136.62	128.87	105.26
Minimum (mg/kg)	98.82	85.44	75.61
Mean (mg/kg)	107.36	102.10	92.60
Std. (mg/kg)	14.10	14.78	12.40
C.V.	0.13	0.14	0.13

Table 4. *Mean values of REEs indicators under different forest types*

Indicators	GL	LL	RL
LREE (mg/kg)	72.12	67.14	59.91
HREE (mg/kg)	35.24	34.96	32.69
LREE/HREE	2.05	1.91	1.83
δEu	0.86	0.98	1.01
δCe	1.24	1.31	1.83
La/SmN	5.00	4.82	5.89
Gd/LuN	1.47	1.46	1.19
Gd/YbN	1.24	1.30	1.01

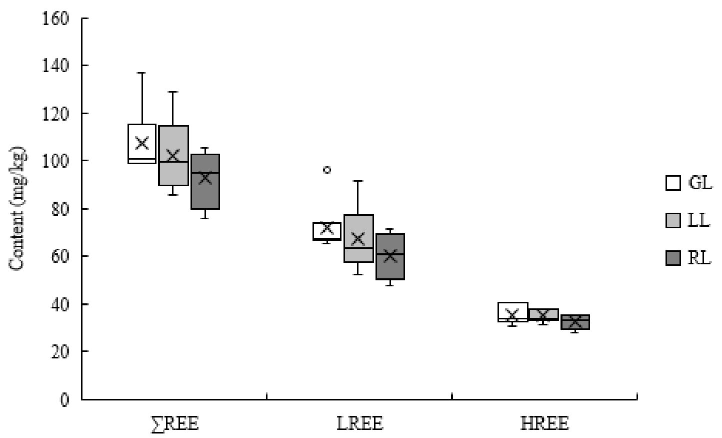

Figure 4. *Statistical values of ∑REE, LREE, HREE under different forest types*

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Correlations among REEs

There are positive correlations among LREEs and HREEs, which indicates good synergistic effects among REEs (*Fig. 5*). In terms of LREEs, La shows a highly significant positive correlation with Ce, Pr, Sm, and Y ($p < 0.01$), Ce shows a highly significant positive correlation with La, Pr, and Sm ($p < 0.01$), Nd shows a highly significant positive correlation with La, Ce, and Sm ($p < 0.01$); and in terms of HREEs, Er shows a highly significant positive correlation with Tm, Yb ($p < 0.01$), and Ho and Lu ($p < 0.05$); Er and Tm are negatively correlated with LREEs, with a significant negative correlation with Pr and Sm ($p < 0.05$).

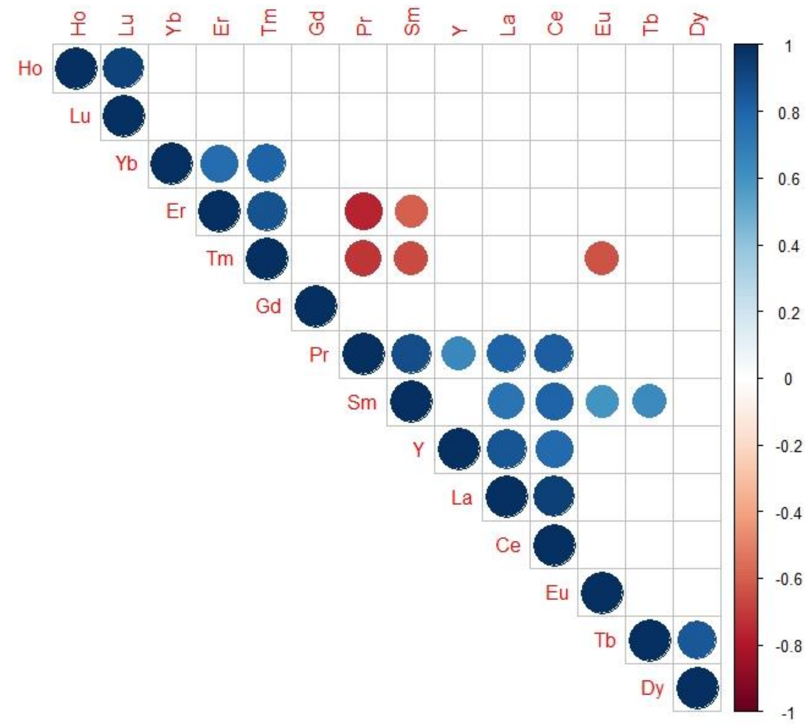

Figure 5. *The correlations between various REEs*

Correlation between REEs and pH values

The relations between the REEs indexes and pH value are significant (*Fig. 6*). The pH value is positively correlated with ∑REE ($p < 0.01$), LREE, HREE, and LREE/HREE ($p < 0.05$), while negatively correlated with δEu and δCe ($p < 0.05$).

Discussion

The content of REEs in soil is mainly related to parent material, process of soil formation, and clay content. Soil-forming process is an important factor affecting the content of REEs in soil. In different soil-forming processes, the enrichment and leaching migration of REEs in the surface layer are different. The lateritic and red soils in southern China have a deep soil-forming process and a strong relative enrichment of REEs, but the low pH value of the soil and the small adsorption capacity of REEs increase the leaching and migration ability of REEs in the soil. Although the formation

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process of neutral and calcareous soils in northern China is shallow and the enrichment of REEs in soils is relatively weak, their migration ability in soils is low. Especially under this soil condition, Ce is easy to be oxidized and hydrolyzed to form Ce(OH) with low solubility and precipitation, resulting in enrichment in the surface layer of black soil and black calcium soil (Ran and Liu, 1994).

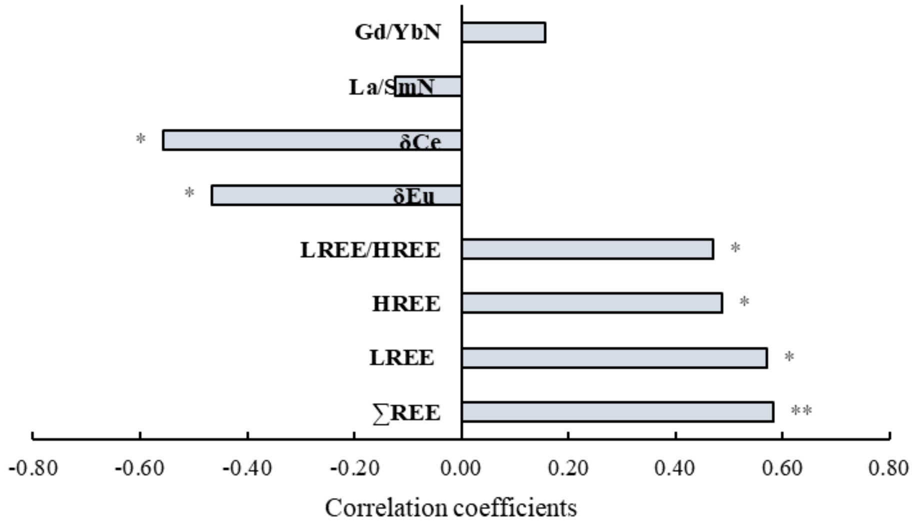

Figure 6. *Correlations between REEs indicators and pH values (*P < 0.05, **P < 0.01)*

REEs content

The ∑REE in the *Larix gmelinii* forest soil is 102.04 mg/kg, lower than the national mean value of China. In general, the ∑REE in China decreases gradually from south to north. The study area is located in the cold temperate zone, so the ∑REE is low. In this study, the determination of REEs is based on the soil after 2 mm sieving, which belongs to the whole soil data, while other related RE determination is mostly based on 0.1-0.2 μm sieving data. Zhang et al. (2018) studied REE contents of < 75 μm and < 5 μm silicate fractions in ten deserts and sandy lands of northern China. The results showed that the smaller the particle size of soil, the higher the REE content. So, it is normal that the element content is lower than other research results. The ∑REE in all kinds of soils was compared with the national mean values (Wei et al., 1991). The results showed that the ∑REE in aeolian sandy soil, chestnut calcareous soil, brown desert soil, brown coniferous forest soil, oasis soil, and grey brown desert soil were very significantly lower. While the brown coniferous soil is mainly distributed in our study area. The geochemical behaviors of REEs are different because of their differences in electronic configuration and ion radius. Compared to HREEs, LREEs are more difficult to migrate and relatively enriched. The study area is located in the cold temperate continental climate zone, where rainfall is concentrated and temperature is low, chemical weathering and biological effects are rather weak, and trace elements in soil are not easy to migrate. The REEs content is lower than that in other areas.

The pH value has a great influence on the release, migration, and enrichment of REEs (Huang and Gong, 2001). Under acidic and weak acidic conditions (pH < 7), REES mainly migrates in the form of soluble cations (Chen et al., 2011). REEs solubility is greatly influenced by pH, with REEs concentration increasing with

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decreasing pH (Elderfield et al., 1990; Astrom, 2001). For pH 3.5-7.5, REEs behavior is mainly controlled by ion exchange and adsorption of Fe and Mn-oxyhydroxide loads (Elderfield et al., 1990). The soil pH value in study area is between 4.5 and 6.5, which belongs to weak acidic soil.

The content of HREE is close to the national mean value, while the content of LREE is lower than the national mean value. The correlation analysis of rare earth elements in pH value shows that there is a significantly positive correlation between pH value and the content of LREE. The soil in the study area is acidic, and the pH value is between 4.5 and 6.5, so the content of LREE is low. The LREE/HREE ratio is 1.95, which is lower than the national mean value (3.1). This is related to the soil parent material in this area. It also reflects the weakly chemical weathering in this area. The fine parts of the soil rich in LREEs (such as clay minerals) are migrated by wind, and the LREE is obviously low.

The contents of Al_2O_3, K_2O, CaO, and Na_2O were also determined, and the CIA values of each point were calculated by converting their contents into molar contents. The results show that the minimum, maximum, and mean CIA is are 58.9, 73.8, and 64.6, respectively. According to the literature (Feng et al., 2003), the CIA value ranges from 50 to 65, reflecting the weakly chemical weathering under cold and dry climate conditions, which means that the surface soil of the study area is weakly affected by chemical weathering, which is not conducive to the fractionation of REEs.

The three forest types distribute at different altitudes in study area. The GL forest has the lowest elevation and the RL forest has the highest elevation. The soil in study area is acidic (pH < 6.5), the LREEs are easily leached. As rainfall, the REEs are easily washed out on the slope and accumulated in the lower part, which makes the REEs content higher in lower slop than upper slop (Fu et al., 2000).

Anomaly characteristics

Ce and Eu are variable valence elements. Ce has two valence states of + 3 and + 4, and Eu has two valence states of + 2 and + 3. Under weak acidic conditions, Ce^{4+} is easy to hydrolyze and stay in place, resulting in a positive anomaly of Ce (Marker and De Oliveria, 1990). Under reduction conditions, part of Eu^{3+} is reduced to Eu^{2+} (Chen et al., 2011), Ce^{4+} is easily deposited in the upper layer of the weathering crust and separated from other REEs; Eu^{2+} is easily leached from the upper layer of the weathering crust, therefore besides the influence of parent rock, δCe and δEu values can reflect the degree of soil weathering to some extent (Wei et al., 1991). Because the leaching of soil in the south is stronger than that in the north, the δEu value in forest soils in China increases gradually from south to north. The values of δCe and δEu in study area are higher than the national mean values (1.22 and 0.92). The correlation analysis between REEs and pH values showed that there was a significant negative correlation between pH and δCe, δEu. While the pH value in study area was lower, so the δCe and δEu values were higher. As a general rule, δEu values do not become fractionated during chemical weathering and transportation processes (Mclennan, 1989).

Profile characteristics

Leaching is the main process of forest soil formation (Wei et al., 1991). Due to the effect of rainfall and infiltration, REEs, like other soluble substances, are leached and

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easily migrate to the lower part of soil profile, especially in acid soil environment. The surface layer of soil is often depleted by strong leaching, while the leached REEs are infiltrated downward and accumulated in the deep soil (Wang et al., 2012). Therefore, the distribution of REEs in soil profile generally increases with depth (Wei et al., 1991; Sheng, 2011), showing a distribution pattern of low to high (Fu et al., 2000). However, due to the low temperature and precipitation in study area, REEs' surface migration is more obvious than other layers.

δEu and δCe reflect the fluctuation characteristics of Ce and Eu during soil development (Sheng, 2011). There is a certain relationship between the anomaly degree of Ce and the maturity of soil, and the weathering process has a trend to positive Ce anomaly. Because of the strong weathering and the high maturity of the upper soil layer, the Ce in the upper soil presents positive anomaly; because of the strong acidity, the leaching and migration ability of most REEs increases in the surface soil layer (Wang et al., 2012), the surface REEs are easy to migrate, and the Ce is enriched in the lower layer (Sheng, 2011). The Eu deficit in the surface layer is weaker than that in the lower layers, which may be related to the redox reaction during soil development.

Conclusions

The mean content of REEs in the *Larix gmelinii* soil is lower than the national and global average, and it follows the Oddo-Harkins rule, the soil environment is basically safe under human disturbance. There is a certain differentiation phenomenon between LREEs and HREEs, with LREEs and Ce relatively enriched. There is also a certain fractionation between LREEs and HREEs. The total amount of REEs shows an increasing trend with the depth of the soil profile, and tends to be gradual after 20 cm. The content of REEs in the three types of forest soils is higher in GL > LL > RL, among which the difference in LREEs is greater than that in HREEs. There is an overall positive correlation between LREEs and HREEs, indicating a good synergistic effect. The relationship between each characteristic value and pH value is significant, with ∑REE, LREE, HREE, LREE/HREE and pH value showing a significant positive correlation, δEu, δCe and pH value showing a significant negative. The research results can provide basic data for in-depth analysis of environmental safety risks of *Larix gmelinii*. REEs have shown many positive effects in the agricultural field, but their mechanisms of impact on plants are still unclear. In the future, in-depth research should be conducted on the mechanism of REEs and plant growth, in order to provide new avenues for sustainable forestry development.

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