Study on Speciation Chemical Analysis of Rare Earth Elements in Soil Based on Green Environmental Technology

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Abstract. The impact of rare earth elements on the soil environment is not only related to its total amount, but also more closely related to its chemical form. The green and environmentally friendly acid digestion and morphological continuous extraction methods were used to extract and analyze the total amount of rare earth elements and the forms of rare earth elements in the soil samples. Inductively coupled plasma mass spectrometry was used to determine the content of rare earth elements and the content of rare earth elements in the soil samples. Form content. The results show that the content of rare earth elements in the collected soil samples is 200-1418mg/kg, and the content of light rare earth elements is much higher than that of heavy rare earth elements; the recovery rate of the sum of the combined forms of rare earth elements relative to the total amount is 88.2% to 110%, indicating that the continuous extraction method is suitable for the analysis of rare earth elements in soil samples. The rare earth elements in soil samples mainly exist in the residue state, which is 33%-80%; the co-precipitation state of crystalline iron and manganese hydroxide is 10%-31%; the adsorption state of humus and amorphous oxide is 5.0%-18%; The exchange state and the carbonate combined state are 4.0% to 23%; the amorphous iron-manganese oxide co-precipitation state is less than 3%. The influence of the location of the sampling point and the nature of rare earth elements on the content of rare earth elements was analysed, and the influence of soil properties on the distribution of morphology was discussed.

Keywords: Green environmental protection technology, continuous extraction, rare earth elements, speciation analysis, soil.

1. Introduction
My country is a large country of rare earth resources, with reserves accounting for about 80% of the world. Beginning in the 1970s, my country began to apply rare earth elements to agricultural production. By the early 1990s, the cumulative area of agricultural use of rare earth elements reached 93 million mu. At present, rare earth micro-fertilizers are still widely used in agriculture and forestry production. However, the ecological and environmental effects formed after the exogenous rare earths enter the soil have gradually attracted attention, and it is generally recognized that the low concentration of rare earth elements promotes the growth and quality of plants, the inhibitory effect at high concentrations, and the effects on animals. The effects of physiological and reproductive
processes. In view of this, the environmental problem of rare earth elements has become another new environmental hot spot after the environmental problems of heavy metal elements and persistent organic pollutants. To systematically and comprehensively solve the ecological and environmental problems of rare earth elements, we must first understand and master the soil [1]. Geochemical behaviour of rare earth elements. On the other hand, the content of rare earth elements in the soil directly affects the agricultural effects of rare earth elements. Therefore, research on the background value content and distribution of rare earth elements in the soil is positive for adopting reasonable regulation of the supply level of rare earth elements and promoting the agricultural use of rare earth elements significance. The adsorption and desorption of heavy metals and rare earth elements on the surface of iron-manganese oxide minerals in soil, weathered crust and surface sediments has been considered as one of the important mechanisms of element activation, migration and pollution in the superficial environment. The morphological classification study of rare earth elements shows that the rare earth elements in the soil mostly exist in the form of iron and manganese oxides combined.

2. Materials and methods

2.1. Sample collection
In July 2018, at 12 sampling points in the upper reaches of the Yellow River (Table 1), a portable sediment sampler was used to collect 1kg of surface sediment samples with a thickness of 5-10cm, placed in a sealed plastic container, and stored in a portable refrigerator below 4°C.

Table 1. Soil sample information table.

| sampling time | Altitude/m | pH  | TOC/% |
|---------------|------------|-----|-------|
| 2018.07.16    | 998±5      | 9.25| 0.16  |
| 2018.07.16    | 1011±7     | 9.06| 0.41  |
| 2018.07.17    | 1055±12    | 8.99| 0.34  |
| 2018.07.17    | 1084±4     | 8.98| 0.30  |
| 2018.07.18    | 1079±7     | 9.01| 0.44  |
| 2018.07.19    | 1102±6     | 8.95| 0.40  |
| 2018.07.19    | 1133±6     | 9.08| 0.27  |
| 2018.07.19    | 1147±5     | 9.04| 0.27  |
| 2018.07.21    | 3410±7     | 8.52| 2.27  |

2.2. Sample collection and processing
In this study, 6 typical sampling sites were selected to collect surface or farming layer (within 0-20cm) soil, mix them with multi-point sampling method, remove debris, plant roots, biological debris and other impurities, dry them naturally, and mix them evenly. Use the quarter method to take 25g sample, grind it fully in an agate mortar, pass a 200-mesh sieve, and store it in a sample bag for analysis and testing.

2.3. Experimental method
The analysis of rare earth element content adopts the closed acid solution method. Weigh 25mg of sample into the inner tank of the closed sample dissolver, add 1mL of hydrofluoric acid, 0.5mL of nitric acid, and seal. Put the sample dissolver into the oven and heat it for 24h, the temperature is controlled at about 185±5℃. After cooling, take out the inner pot, place it on a hot plate and heat at 120℃ to evaporate, then add 0.5mL of nitric acid to evaporate, and repeat this step once. Add 5mL of 50% nitric acid, seal again, put in an oven, and heat at 130℃ for 3h. After cooling, take out the inner tank and transfer the solution to a plastic bottle [2]. Dilute with water, dilute to 50mL, shake well, and determine the concentration of 15 elements of lanthanide (except Pm) and yttrium (Y) by inductively coupled plasma mass spectrometry (ICP-MS). Quality monitoring is carried out by standard materials (GBW07402, GBW07430, GBW07158, GBW07161), and the measured values of rare earth elements
of the standard materials are all within the range of (certified value ± uncertainty), which meets the research needs.

The rare earth element form extraction adopts the European Union BCR sequential extraction method, which is simple to operate and has good reproducibility. The rare earth elements are divided into weak acid extraction state, reducible state, oxidizable state, and residue state. ICP-MS was used to determine the content of rare earth elements in 6 soil samples. In the process of sequential extraction of BCR, the international standard material BCR-701 was used for quality monitoring. The analysis errors of Cd, Cr, Cu, Ni, Pb, and Zn were all less than 20%, which verified the reliability of the method. The sum of the four phase states of the rare earth elements in the 6 samples is consistent with the total content value within the error range, and the recovery rate of rare earth elements is between 82.8% and 115.8%, which meets the needs of research work.

The working parameters of ICP-MS in the rare-earth element test process are shown in Table 3. The standard solution used for the computer analysis is a mixed standard solution of each element, which is prepared by diluting each single element standard material step by step. The best tuning solution for mass spectrometry is 2μg/L Li, Be, Co, In, Bi, U standard solution, and the internal standard solution is 10μg/L Rh and Re mixed solution. The chemical treatment and computer testing of soil samples were all completed at the National Geological Experiment and Testing Centre.

| Working parameters | Set conditions | Working parameters | Set conditions |
|--------------------|----------------|--------------------|----------------|
| ICP power          | 1300W          | measurement method | Peak jumping   |
| Cooling air flow   | 13.0L/min      | Scan times         | 50             |
| Auxiliary air flow | 0.75L/min      | Residence time/channel | 10ms          |
| Atomizing gas flow | 1.0L/min       | Number of channels per mass | 3 |
| Sampling cone aperture | 1.0mm            | Total acquisition time | 48s          |
| Truncated cone aperture | 0.7mm             |                     |               |

Table 2. ICP-MS working parameters.

2.4. Analysis method

2.4.1. Determination of REE form and TOC content. The analysis sample after the morphology extraction was tested according to the DZ/T0223-2001 method and HR-ICP-MS under fully automatic optimized tuning conditions; the TOC content was determined according to the SY/T5116-1997 method.

2.4.2. Fractionation of REE. The change in the relative abundance of REE in different media is called fractionation. This fractionation has been proved to be very important in explaining the formation of rocks, and it cannot be ignored for the distribution, migration, transformation and fate of REE in the environment. Meaning. The main indicators of fractionation include standardized diagrams of chondrites, fractionation coefficients (that is, the ratio of light to heavy rare earth elements, L/H), and abnormal coefficients of europium and cerium. The calculation of europium and cerium anomaly coefficients uses the following formula.

\[
\delta_{\text{Eu}} = \frac{E_{\text{u}}}{\sqrt{Sm} \times \text{Gd}}
\]

\[
\delta_{\text{Ce}} = \frac{C_{\text{e}}}{\sqrt{La} \times \text{Pr}}
\]

In the formula: \( \delta_{\text{Eu}}, \delta_{\text{Ce}} \) is the abnormal value of elements Eu and Ce respectively, and \( E_{\text{u}}, S_{\text{m}}, G_{\text{d}}, C_{\text{e}}, L_{\text{a}}, P_{\text{r}} \) is the ratio of the measured value of each rare earth element to the
standard value of chondrite. If $\delta_{Eu} (\delta_{Ce}) > 1.05$, then Eu (Ce) is positive anomaly, which means Eu (Ce) is enriched; if $\delta_{Eu} (\delta_{Ce}) < 0.95$, it means Eu (Ce) is deficient.

3. Results and analysis

3.1. The relationship between the morphology of iron and manganese oxides and the content of rare earth elements

Many studies have shown that rare earth elements in the soil will be combined with iron and manganese oxides, but there are few studies on the contribution of different forms of iron and manganese oxides to the combination of rare earth elements. In this study, based on the content of DCB extracted and ammonium oxalate extracted iron and manganese oxides in paddy soil and fluvo-aquic soil, the correlation with the content of light rare earths, heavy rare earths, and total rare earths and their relative contribution rates were discussed. It can be seen from the results in Table 3 that the iron oxide system in paddy soil and fluvo-aquic soil is more closely related to the rare earth content in paddy soil and fluvo-aquic soil than that of manganese oxide system. The content of free iron oxide, especially the crystalline iron oxide therein, has a very significant (p<0.01) correlation with the content of light rare earth ($\delta_{Ce}$), the content of heavy rare earth ($\delta_{Eu}$) and the total amount of rare earth ($\delta_{REE}$). From the comparison of the correlation coefficients, the free iron oxides have a greater impact on the abundance of rare earth elements in the fluvo-aquic soil than on paddy soil. This may be due to the relatively sandy texture of the fluvo-aquic soil and the greater storage capacity of the elements in the soil. Poor, so the combination of iron oxides is more obvious for the preservation of rare earth elements in fluvo-aquic soil [3].

The rare earth elements combined in amorphous iron oxide and crystalline iron oxide may be mainly light rare earth elements, which is basically consistent with our analysis of paddy soil. Although free iron oxide also has a very significant correlation with the total amount of heavy rare earths, the correlation coefficient with free iron oxide is lower than that with the total amount of light rare earths. In this study, amorphous iron was not found to have a significant correlation with the content of rare earths, but the content of non-free manganese and active manganese has a significant positive correlation with heavy rare earths. The situation in fluvo-aquic soil is slightly different from paddy soil. The combination of free iron oxide and heavy rare earth is stronger than that of light rare earth.

| Rare earth | Iron oxide Fed | Feu | Feo | Fec | Mnd | Mnu | Mno | Mnc |
|------------|----------------|-----|-----|-----|-----|-----|-----|-----|
| Paddy soil | *0.479*** | 0.024 | 0.054 | 0.443** | –0.093 | 0.127 | –0.025 | –0.143 |
| Eu         | *0.382*** | 0.331** | 0.194 | 0.301** | 0.113 | 0.417** | 0.204* | –0.073 |
| REE        | *0.485** | 0.07 | 0.077 | 0.440** | –0.066 | 0.176 | 0.008 | –0.139 |
| Chao soil  | *0.662*** | 0.222 | 0.274 | 0.623* | –0.009 | 0.093 | 0.203 | –0.185 |
| Ce         | *0.812*** | 0.226 | 0.313 | 0.771** | 0.053 | 0.156 | 0.295 | –0.16 |
| Eu         | *0.702** | 0.225 | 0.285 | 0.662** | 0.005 | 0.108 | 0.226 | –0.181 |

3.2. Morphological analysis of REE in surface sediments

Speciation analysis is an analysis process that characterizes and measures various chemical and physical forms. The bioavailability of the element in the environment or the ability to accumulate in the organism or the toxicity to the organism is closely related to the physical and chemical forms of the element. At present, the multi-stage continuous extraction methods used in REE morphological
analysis mainly include Tessier method and BCR method. The comparative experimental results of the Tessier method and the improved BCR method in many laboratories in China show that the improved BCR method is simplified in operation and has good reproducibility. The forms of elements are mainly divided into weak acid extraction state, reducible state, oxidizable state and residue state. The weak acid extraction state includes water-soluble state, exchangeable state and carbonate-bound state. Rare earth elements in this form are easily released into the water body, migrate and produce bioavailability; the reducible state is mainly the iron-manganese oxide-bound state. When the pH of the environment where the rare earth element is located is less than 7, the rare earth element is easily hydrolysed and complexed with the hydroxyl group of the iron manganese oxide, which has certain biological effectiveness; the oxidizable state mainly includes the organic matter bound state and the sulphide bound state, and strong oxidants Released under conditions, its stability is higher than that of the weak acid extraction state, and it has potential bioavailability and migration ability; the residue state mainly exists in the crystal lattice of silicate, primary and secondary minerals, and is difficult to be used by biology [4]. The modified BCR continuous extraction method was used to pre-treat the surface sediment samples, and the REE content in each form was determined and analysed by HR-ICP-MS (Figure 1).

Figure 1. Comparison of the distribution patterns of rare earth elements in the cross-section of fertilized paddy soils with different iron and manganese oxide contents.
3.3. REE fractionation in surface sediments

It can be seen from Fig. 2 that (1) The standardized distribution curve of the chondrites of the REE and the average REE of the upper reaches of the Yellow River at each sampling point has the same trend, and is similar to the Chinese soil background, the average value of the entire Yellow River, and the distribution patterns of North American shale. Tilting to the right, showing enrichment of light rare earth elements; (2) The normalized value of REE in the surface sediments of each sampling point is higher than the average value of the entire Yellow River. Compared with the Chinese soil background, the REE content in the surface sediments of the sampling site (S1) and the sampling site (S8) are higher than that of the Chinese soil background. The La and Ce of other sampling sites are relatively low, but the content of heavy rare earth elements is slightly less. High and Chinese soil background; (3) According to the L/H, δEu, δCe and other related characteristic parameters of the 12 sampling points in Table 3, it can be seen that: L/H is distributed between 7.51 and 9.45, indicating The degree of fractionation of light and heavy rare earth elements is obvious; the δEu of each sampling point is between 0.56 and 0.93, with an average value of 0.75, showing a weak to moderate negative Eu anomaly. The degree of anomaly is similar to the Chinese soil background (0.65). Is similar, indicating that the main source of rare earth elements in sediments is soil weathering. δCe is distributed between 0.88 and 0.97, with a mean value of 0.93, indicating that Ce presents a weak negative anomaly. Because Ce anomalies generally occur during rock weathering under weakly acidic conditions, the pH under the conditions of this study is alkaline, indicating that the surface sediment environment does not have the conditions for Ce anomalies.

![Figure 2](image-url)

**Figure 2.** Distribution curve of rare earth elements in soil samples.

3.4. Eu deficiency and Sr loss in paddy soil and fluvo-aquic soil under the influence of iron freeness

Since the ionic radius of the divalent Eu and the ionic radius of the divalent cation Sr are both around 1.2 (1nm=10), the chemical behaviour is very close, and Sr is more likely to be leached in the soil. Therefore, if Eu is reduced from trivalent to divalent in the soil, it is likely to be leached together with Sr. We performed a linear correlation fit between Eu and soil Sr content in paddy soils and fluvo-aquic soils in the Yangtze River Delta and the Pearl River Delta, and showed that the δEu and soil Sr content in the Pearl River Delta have a very significant linear correlation (p<0.01), and the two cannot be linearly fitted in the soil of the Yangtze River Delta. Further analysis of the freeness of iron and manganese oxides and the content of Sr in the soils of the two regions showed that the freeness of iron oxides in the soils of the two regions was significantly different. The freeness of iron in paddy soil and fluvo-aquic soil in the Pearl River Delta region was mostly in the iron freeness in paddy soil and...
fluvo-aquic soil in the Yangtze River Delta is below 50%. Correspondingly, the content of Sr in the soil is just the opposite. The content of Sr in the soil of the Pearl River Delta is mostly below 100 mg kg\(^{-1}\), while the content of soil in the Yangtze River Delta is more than 100 mg kg\(^{-1}\) (Figure 3). It can be seen that in the soil with high iron oxide freeness, the soil Sr element will be leached along with the reduction of Eu, and as the soil iron oxide freeness decreases, this correlation will decrease or even decrease. No. It may be due to the fact that the fractionation mechanism of Eu under low iron freeness is different from that of high iron free soil. For example, the adsorption and desorption of rare earth elements by manganese oxide or low molecular weight organic acids such as acetic acid and citric acid may be a deficiency of Eu fractionation. The main influencing factors [5].

![Figure 3](image)

Figure 3. Comparison of the freeness of iron manganese oxide and Sr content.

4. Discussion
The mining of rare earth minerals will cause a large amount of rare earth elements to migrate and transform into the soil around the mining area, causing environmental pollution. The bioavailable state of rare earth elements mainly refers to the weak acid extraction state. Long-term accumulation in the soil environment will destroy the soil ecosystem and endanger the health of animals and plants. Therefore, it is necessary to attach great importance to the soil environmental pollution caused by the development of rare earth resources and effectively prevent them. In the metal pollution of rice fields, the main source of rare earth elements is tailings slag, which is diffused with precipitation and strong wind, and exists in the form of independent minerals in the soil. In each form, it is mainly in the form of residues, accounting for about 64.0%~89.4% of the total rare earth elements. At present, there are relatively few studies on the control of soil pollution around the Baiyun Obo mining area. The control measures are mainly prevention, such as the establishment of a slag field or a slag bank to store mining waste residues, etc., to reduce environmental pollution by suppressing dust flying. The contaminated soil around the mining area is rich in heavy rare earth elements, and their main existence in the soil is weak acid extraction and reducibility, such as JXS-1, JXS-2, and JXS-3. The ratio of weak acid extraction of rare earth elements to the total rare earth elements, it is about 16.6%, 9.12%, 21.0%, with high mobility and biological activity. In combination with the acidity and strong viscosity of red soil in the southern region, the main recommendations for the treatment of contaminated soil are the combination of chemical improvement and biological improvement. First, chemically ameliorate the contaminated soil, add natural mineral modifiers such as montmorillonite, attapulgite, etc., to adjust the pH of the soil, so that the rare earth elements will undergo adsorption, oxidation-reduction, and precipitation reactions, and transfer from a weak acid extraction state to an oxidizable state. Reduce its bioavailability. Secondly, carry out biological improvement of contaminated soil, by
selecting microorganisms or plants with strong extraction capacity and high accumulation of rare earth elements to transfer rare earth elements to organisms, thereby improving the soil environment and returning the content of rare earth elements to a "safe" level.

5. Conclusion
Through the determination and analysis of the total amount of rare earth elements, the content of rare earth elements in the farmland soil of this rare earth mining area is much higher than the median value of the content of rare earth elements in the soil of our country and the earth content of the world. It is relatively rich in heavy rare earth elements, the rare earth element yttrium (Y) The content is relatively high, belonging to yttrium-rich rare earth ore, and the addition of different shapes of zeolite has no effect on the total content of rare earth elements in the soil, but the total amount of rare earth elements does not fully indicate its effectiveness and potential for soil organisms. The strength of migration. Therefore, it is necessary to study the morphological distribution characteristics of rare earth elements in the soil of the mining area to further illustrate the effectiveness and potential harm of the rare earth elements migrated from in-situ leaching of rare earth mines to surrounding farmland soil organisms and crops.

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