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Geochemical background and dispersion pattern of the world's largest REE deposit of Bayan Obo, China



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ABSTRACT

The Bayan Obo deposit is the largest deposit of rare earth elements (REEs) in the world, with its light REE (LREE) reserve constituting approximately 45% of the world's total LREEs. This study identifies the geochemical background of REEs in the Bayan Obo region and investigates REE dispersion pattern along a stream, the fractionation between parent rocks and soils, as well as REE distribution in a weathering profile, to reveal the geochemical behavior of REEs during hypergene processes in semi-arid grasslands. Results show that the REE content in the slates of the Bilute, Jianshan, and Dulahala Formations, which are surrounding rocks of the Bayan Obo deposit, is far higher than those observed in ordinary slate and the continental crust of the North China Craton. These surrounding rocks may have provided sufficient REE sources to form the current, huge REE deposit. The total REE content of stream sediments in the Bayan Obo region ranges from 46.9 to 799.8 μ g/g, with a median of 170.8 µg/g. Two large-scale REE anomalies were discovered to the west of the Bayan Obo region. The REE content in soil is primarily determined by the parent rock, and no fractionation occurs between heavy REEs (HREEs) and LREEs after the parent rock weathers in semi-arid grasslands. Across the soil profile in Bayan Obo region, REEs typically enrich the surface and deep layers; the middle layer typically contains low REE content owing to the existence of caliche. Along streams, REEs primarily migrate with fine-grained particles over long distances (7 km or longer) via mechanical means. In contrast, coarse-grained particles mainly remain in situ, Affected by aeolian sand, the REE content is relatively low in the 40-80 mesh fraction.

1. Introduction

The International Union of Pure and Applied Chemistry defines rare earth elements (REEs) as 15 lanthanides on the periodic table with atomic numbers ranging from 57 to 71 together with yttrium and scandium, which are included in this list as they are chemically and physically similar to and closely associated with lanthanides. As REEs are increasingly used in hi-tech applications such as magnets, catalysts, metal alloys, electronics, glass, ceramics, and new materials, they are defined as critical mineral resources by the IUGS Resourcing Future Generations initiative (Alonso et al., 2012; Dutta et al., 2016; Zhou et al., 2017) and described as critical at-risk marketable elements in the British Geological Survey Risk List (2015).

Currently, China hosts 42% of the world's total REE reserve base and contributes > 80% of the world's REE production; this contribution

exceeded 95% before 2012 (Dutta et al., 2016). More than 80% of light REE (LREE) resources in China are distributed in the Bayan Obo region (Hong-Rui, 2016).

The Bayan Obo Fe–REE–Nb deposit is located at the northern margin of the North China Craton (NCC), approximately 150 km north of Baotou City, Inner Mongolia, China. It is the largest REE deposit in the world, the second-largest niobium (Nb) deposit in the world, and a huge iron (Fe) deposit in China. Within this deposit, at least 90% of the REEs exist as separate minerals, predominantly as LREE minerals, such as monazite and bastnaesite, which are mainly mined through opencast operations (Wang et al., 2019). Thus far, research in the Bayan Obo region has mainly focused on the genesis and exploitation of this deposit (Hong-Rui, 2016; S. Liu et al., 2018; Y. Liu et al., 2018; Smith et al., 2015; Sun et al., 2014; Yang et al., 2017; Zhou et al., 2018; Bai, 2012; Yang et al., 2015). Attention has also been paid to the soil and

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environmental aspects of the REEs (Pan and Li, 2015; Duan, 2012; Guo et al., 2013; Lin et al., 2017).

Systematic geochemical mapping has been performed worldwide since the first geochemical atlas was published (Wang et al., 2016; Darnley, 1995; Darnley, 1997; David, 2012; de Caritat et al., 2008; de Sá Paye et al., 2016; Demetriades et al., 2015; Goodenough et al., 2016; Mihajlovic and Rinklebe, 2018; Reimann, 2005; Sadeghi et al., 2013a; Sadeghi et al., 2013b; Sklyarova et al., 2017; Smith et al., 2011; Wang et al., 2015; Xuejing and Hangxin, 2001). However, the determination, background, and distribution of all REEs have received little attention. In 1978, the "Regional Geochemistry-National Reconnaissance Program" (RGNR) was launched in China; this program has covered an area of 7 million km² at a scale of 1:200,000 to research the above points (Wang, 2013a; Wang, 2013b; Xie, 1992). However, only two REEs, La and Y, have been analyzed under this program, providing very limited information on the REE distribution and background in the Bayan Obo region.

With the exploitation and application of REEs, more REEs are

introduced into the soil, generating a wide array of eco-environmental concerns in this area (Wang et al., 2019). Several ecotoxicological effects of REEs have been observed: Gd can cause kidney failure, anaphylactic shock, and even cause death (Mihajlovic et al., 2017). The potential toxicity of REEs in soils depends on many factors such as concentration and the mobility of the elements during hypergene processes (Aubert et al., 2002; Compton et al., 2003; Laveuf and Cornu, 2009; MAO et al., 2009; Miao et al., 2008; Mihajlovic et al., 2014; Šmuc et al., 2012; Xiao et al., 2016). Therefore, the natural background and distribution of REEs must be defined to distinguish their natural variations related to geology from mineralization and contamination (Fedele et al., 2008).

The main objective of this study is to identify the geochemical background and distribution of REEs in the Bayan Obo region and investigate the REE dispersion pattern along a stream together with the fractionation between parent rocks and soils and distribution in a soil profile to reveal the geochemical behavior of REEs during hypergene processes in a semi-arid grassland.



Fig. 1. Geological setting of the Bayan Obo district.

(Modified from 1:200,000 geological map and the work of Hong-Rui (2016), S. Liu et al. (2018), and Y. Liu et al. (2018).)

2. Geological background and landscape of the study area

2.1. Geological background

The Bayan Obo deposit, as one of the world's rare polymetallic deposits, spans a length of 18 km from east to west and is approximately 3 km wide. This deposit lies on the northern margin of the NCC, bordering the Central Asian Orogenic Belt on the north. It is hosted by Paleo- to Mesoproterozoic rocks of the Bayan Obo Group, which uncomfortably overlies the basement complex (Hong-Rui, 2016; S. Liu et al., 2018; Y. Liu et al., 2018; Zhu et al., 2015; Wang et al., 2018) (Fig. 1). Based on iron grade (TFe > 20%), the Bayan Obo deposit can be separated into three major ore bodies: the Main, East, and West orebodies (Fig. 1).

Regional exposures in the Bayan Obo area include the Archean–Paleoproterozoic basement complex, the Paleo- to Mesoproterozoic Bayan Obo group, and Paleozoic and Mesozoic sediments (Hong-Rui, 2016). The Bayan Obo group comprises Bilute, Halahuogete, Jianshan, and Dulahala formations, which contain sandstones having low-grade metamorphism, siltstones, slates, limestones, and dolomites. The Silurian comprises the Upper Bateaobao Group's Haliqi and Aibugaihe formations, containing quartz sandstones, slates, tuffs, andesites, and marbles that are mainly distributed to the northeast of the deposit. Upper Jurassic sandstones and shales are mainly found in this northeastern part.

Regionally, the Bayan Obo area has experienced four stages of magmatism: Wutaian–Luliangian, Caledonian, Variscan, and Yanshanian (Yang et al., 2015). Middle Variscan biotite granite, granodiorite, Late Variscan biotite granite, and gneissose biotite granite are widely distributed in the study area (Fig. 1).

2.2. Geomorphic landscapes

The study area lies to the south of the Mongolian Plateau in an inland arid climate zone. Affected by strong cold air from Siberia, Lake Baikal, and Ondorhaan, the study area's climate is cold, dry, and windy, with distinct temperature differences. The prevailing annual wind direction is northwest (Gao et al., 2017). The altitude is normally 1000–1100 m above sea level, with relative height differences of 50–200 m (Kong et al., 2004). Soil and stream sediments are commonly blended with aeolian sand. Intense evapo-transpiration has resulted in elevated surface water and groundwater mineralization. Huge accumulations of calcium carbonates, calcium sulfates, and soluble salts in the soil have created an alkaline environment and alkaline barriers (Ren et al., 1984).

3. Methodology

3.1. Sample collection

3.1.1. Rock samples and soils in-situ

Magmatic, sedimentary, and metamorphic rocks from different periods and soils formed through the in-situ weathering of rocks in the study area were systematically sampled to reveal the geochemical background and the REE fractionation between parent rocks and soils (Fig. 1). The main rock types exposed in this area were collected, including sandstone, slate, limestone, marble, and quartzite from the Bayan Obo Group, feldspar quartz sandstone, biotite–plagioclase– hornblende schist from the Silurian Bateaobao Group, rhyolite from the Carboniferous Baoligemiao formation and Jurassic feldspar quartz



Fig. 2. Schematic map of the sample locations along the stream (modified from Google Maps: the blue spots denote sampling locations along the stream and the red spots denote those used to verify whether this area has been contaminated). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sandstone. Variscian biotite granite, granodiorite, and Caledonian finegrained dolomite were also collected.

The soil samples were collected directly from the top of the rock; therefore, it is guaranteed that the samples are the product of in-situ weathering.

3.1.2. Stream sediments

To study the REE dispersion pattern along the stream, research was performed along the northwest direction of the stream from the west orebody of the Bayan Obo deposit (Fig. 1 and the blue spots in Fig. 2). In total, 12 stream sediment samples were collected every 500–800 m starting from the west orebody. Each sample was sieved into five fractions: 4–20, 20–40, 40–80, 80–120, and < 120 meshes.

In addition, 1067 samples of stream sediments, covering about 100,000 km², were collected to investigate the background and distribution of REE near the Bayan Obo region at a sampling density of one sample per 100 km² (Tian et al., 2019; Tian et al., 2018; Wang et al., 2007). The experimental study area was strategically selected to ensure an even distribution of the sampling sites throughout the survey area (Fig. 3), and each sample site was located at a position that can control the maximum area of a sampling cell. Stream sediment samples were collected at the mouths of the streams inside the sampling cell. The samples were collected at depths of 0–20 cm, dried at ambient temperature, and sieved to -100 mesh on-site or in field camps.

3.1.3. Soil profile

Fig. 4 shows the sampled soil profile, about 1 km from the west orebody (E109°50′05.23″; N41°48′48.93). Soil profiles were selected under native vegetation from flat relief to prevent the influence of topography as a dominant factor in pedogenesis. The profile spans about 50 cm from the top to the bedrock and can be divided into A, B, and C horizons. The A horizon comprises yellow–brown soil with a thickness



Fig. 3. Stream sediments sampling sites.

of 0.1 m. It is rich in quartz, feldspar, and clay minerals. The B horizon is rich in clay minerals with a thickness of 0.2 m. It is grey–white in appearance, indicating the existence of caliche. The C horizon is characterized by a loose texture, with a thickness of 0.2 m. The soil profile was collected by a spade. Five samples were collected in the soil profile at about 10 cm intervals from the top to the bedrock. Each of the samples was sieved into five fractions: 4–20, 20–40, 40–80, 80–120, and < 120 meshes.

3.2. Sample preparation

Stream sediment and soil samples were prepared before sending them to the laboratory for analysis. The preparation procedure was as follows: drying (not directly under the sun)—crushing (to prevent the grains clustering into lumps)—sieving (discarding the portion over or lowering the \times mesh)—grinding (samples were ground to a 200 mesh with agate or pure-aluminum-porcelain mill)—splitting and weighing—bottling (polypropylene or plastic bottle)—storing (store the remaining samples in a storage room) (Tian et al., 2019). The rock samples were coarsely crushed to about 1 cm in the jaw crusher, and then finely ground to 200 mesh in the agate or pure-aluminum-porcelain mill, and the subsequent steps were the same those used for the stream sediment samples.

3.3. Laboratory analysis

REE abundances were determined using an inductively coupled plasma-mass spectrometer (ICP-MS) in the Laboratory of Institute of Geophysical and Geochemical Exploration (IGGE), Chinese Academy of Geological Sciences. 0.25 g of the sample was precisely weighed and dissolved in a HF + HNO₃ + H_2SO_4 mixture, evaporated to incipient dryness, and subsequently converted to a 25 ml solution in 5% aqua regia; then, 1 ml clear solution was pipetted out, and diluted to 10 ml



Fig. 4. Soil profile near the west orebody scale.

using 2% HNO₃. Rhodium was used as the internal standard. The detection limits of La and Y were both 1.0 μ g/g, and the detection limits of other REEs were 0.1 μ g/g. The accuracy of the analyses was better than 10%.

Table 1						
Average mineralogical	composition	determined	via X-ray	powder	diffraction	1.

Fraction	Mineral content (%)												
	Quartz	K-feldspar	Plagioclase	Total quartz & feldspar	Illite	Smectite	Kaolinite	Chlorite	Total clay	Calcite	Dolomite	Carbonates	Hornblende
4-20 mesh	36.4	18.8	21.3	76.4	9.2	1.5	1.2	1.0	12.0	9.3		9.3	1.5
20-40 mesh	44.9	19.2	16.5	80.6	5.0	2.2	1.0		7.8	8.1	0.02	8.1	1.0
40-80 mesh	38.7	22.9	22.5	84.1	3.8	1.8	1.4	3.0	7.3	5.1	0.02	5.1	1.0
80-120 mesh	36.3	20.4	24.2	80.9	4.0	3.2	1.3		8.5	6.8		6.8	1.8
< 120 mesh	34.7	15.3	25.4	75.3	5.3	5.2	2.8	1.0	13.8	6.3		6.3	1.8
Bulk size	37.5	20.8	20.4	78.8	7.6	2.2	1.2	1.0	11.1	8.5	0.01	8.5	1.8

X-ray diffraction (XRD) analysis was performed using Rigaku D/ max2500PC in Rock and Mineral Testing Laboratory, Henan Bureau of Geo-exploration and Mineral Development to determine the mineral composition of stream sediments. A quartz glass container was filled with a soil sample and powdered in a mortar. The following parameters were used: a copper anode; K α radiation; X-ray tube voltage, 40 kV; current, 100 mA; 1 mm/8 mm/2.5° filter; diverging slit, 1°; receiving slit, 0.5°; step size, 0.02°; step speed, 2 deg./min.

4. Results and discussion

4.1. Mineralogical composition

The average mineral compositions of different fractions of stream sediments along the river were determined via XRD. Table 1 presents the results for the same.

As can be observed in Table 1, the XRD analysis identified the following mineral phases: quartz and feldspar, which represent 75.3%–84.1% of the total quantity; clay minerals such as kaolinite, illite, smectite, and chlorite, which represent 7.3%–13.8%; carbonate minerals, which represent 5.1%–9.3%. Overall, quartz and feldspar minerals constitute the largest proportion, followed by clay and carbonate minerals.

Fig. 5 shows the total amount of quartz and feldspar exhibiting an inverted "V" distribution pattern, with the highest amount for 40–80 mesh and lowest amount for the coarse fraction (4–20 mesh) and the fine fraction (< 120 mesh). The total amount of clay exhibits an opposite trend with a "U" distribution pattern: the highest amount is observed in the coarse (4–20 mesh) and fine fractions (< 120 mesh).

The total amount of carbonates is the lowest for the 40–80 mesh fraction and relatively high for the coarse and fine fractions.

The relatively high quartz and feldspar content in the 40–80 mesh fraction of the study area is mainly affected by aeolian sand, of which 40–80 mesh is the primary grain size. Microscopic observations of the rounded or semi-rounded shapes of quartz and feldspar in the 40–80 mesh fraction also suggest there is a large amount of aeolian sand mixed. When aeolian sand is blended into the sampled media, the REE concentrations obviously decrease.

4.2. Geochemical background of REE in the Bayan Obo region

4.2.1. REE abundance in rocks in the Bayan Obo region

Rock samples were collected from the study area (Fig. 1). Fig. 6 shows the stratigraphic column and horizons of the analyzed samples in this study.

As can be directly observed in Fig. 6, the total REE content of the Bilute Formation slate (361 μ g/g), Jianshan Formation slate (320 μ g/g), and Dulahala Formation slate (305 μ g/g) of the Bayan Obo Group is the highest. This total REE content is far higher than that observed in either the continental crust (106 μ g/g) (Gao et al., 2004) or the continental crust of the NCC (133 μ g/g) (Yan and Chi, 2005). This REE content is also higher than the total REE content (211 μ g/g) in ordinary slate (Yan and Chi, 2005). The REE content in slate and acidic rocks is higher than that in quartzite, sandstone, and limestone. The slates of the Jianshan Formation and Dulahala Formation, which represent the surrounding rock of the Bayan Obo REE deposit, might have provided sufficient REE sources for forming this huge REE deposit.

The REE content in the Middle Caledonian fine-grained dolomite is



Fig. 5. Mineralogical composition of different fractions (1, 4-20 mesh; 2, 20-40 mesh; 3, 40-80 mesh; 4, 80-120 mesh; 5, < 120 mesh).



Fig. 6. Stratigraphic column of Bayan Obo and REE content in the formations (red triangles denote the sampling horizon; key references used for constructing this column include a 1:200,000 geological map and the work of Zhong et al., 2015; Zhou et al., 2018). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

relatively high compared to other magmatic rocks in the study area. The total REE content of magmatic rocks from any other period is lower than the average value of granite in China (Yan and Chi, 2005).

4.2.2. Geochemical background of REE in stream sediments

A total of 1067 stream sediment samples were collected to investigate the background and distribution of REE in stream sediments (Fig. 2). Figs. 7–8 show interpolated geochemical maps produced with the software GeoExpl2009, using the inverse distance weighted (IDW) algorithm to generate a regular output grid of 10×10 km. The 18-shade color mapped classed are based on the following percentiles of raw data: 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 75, 80, 85, 90, 95, and 97.5. In this paper, we focus on the geochemical maps of total LREE contents and total HREE contents instead of single element because the geochemical maps of LREE (La-Eu) are quite similar, while the distribution patters of HREE (Gd–Lu and Y) are similar.

As can be seen from Fig. 7, high values of LREE are distributed in the east-west direction along Bayan Obo–WulateZhongqi–WulateHouqi. The highest value is located at Bayan Obo deposit. What is striking in this figure is the discoveries of two large-scale REE anomalies to the west of Bayan Obo, which are located to the northeast of WulateZhongqi and to the north of WulateHouqi. The total REE contents are up to 728 µg/g and 432 µg/g, respectively. The main rock type includes the Variscan biotite granite and Bayan Obo Group. Tectonically, it is located in the Bayan Obo rift, the northern margin of the North China Craton, which is similar to Bayan Obo. Notably, the distribution of HREE is significantly different from that of LREE (Fig. 8). Lower values are found for HREE in Bayan Obo, while high values are found approximately 30 km to the west of Bayan Obo.

Basic statistical parameters for REE are presented in Table 2, compared with catchment sediments from the China Geochemical Baselines (CGB) project. The total REE concentrations give a median of 170.8 μ g/ g with a minimum value of 46.9 μ g/g and a maximum value of 799.8 μ g/g. The median value of 170.8 represents the background value of total REE in this area. The total LREE (La–Eu) contents range from 35.3 μ g/g to 704.2 μ g/g, with a median of 130.2 μ g/g, while the total HREE (Sm–Lu and Y) contents range from 11.6 μ g/g to 122.3 μ g/g, with a median of 39.8 μ g/g. Affected by the widely distributed aeolian sand in a semi-arid grassland region, the median value is slightly lower than that of catchment sediments from the CGB project (180 μ g/g).

The highest total REE content (799.8 μ g/g) in this area was found in Bayan Obo deposit. The second-highest total REE content (759.2 μ g/g), which was located approximately 30 km to the west of Bayan Obo, is close to the total REE content in Bayan Obo deposit and 4.3 times of the median value, implying that this area has potentials of harboring undiscovered minerals.

4.3. Fraction of REE in parent rocks and soils

The chemical behavior of rare earth elements is very similar. During the weathering of rocks into soil, rare earth elements will be enriched or lost while light and heavy rare earth elements will be fractionated, which has important geochemical significance. Numerous studies have shown that parent rocks, climatic conditions, pH, Eh, humus, etc. will affect the REE characteristics of soils during weathering. However, the parent rock is often the determining factor for the characteristics of rare earth elements in the soil.

From Fig. 9, we can see that secondary enrichment of REE has occurred in soils formed by the weathering of sandstone, dolomite, and biotite-plagioclase-hornblende schist, and there is slight depletion of the REE in soils formed by the weathering of the slate, while the REE



Fig. 7. Geochemical maps of LREE in Bayan Obo region.



Fig. 8. Geochemical maps of HREE in Bayan Obo region.

- 11 0

Table 2								
Statistical	parameters	of rare	earth	elements	(µg/g)	in	Bayan	Obo

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y	ΣREE	ΣLREE	ΣHREE
Min.	8.9	15.29	2.03	7.24	1.34	0.45	1.17	0.22	1.31	0.23	0.69	0.12	0.8	0.14	6.96	46.9	35.3	11.6
P25	25.8	50	6.38	23.66	4.57	0.94	3.9	0.66	3.79	0.74	2.15	0.35	2.26	0.36	20.21	146.4	111.4	34.7
P50	30.1	58.63	7.47	27.8	5.29	1.06	4.54	0.77	4.35	0.85	2.47	0.4	2.58	0.42	23.43	170.8	130.2	39.8
P75	35.62	69.6	8.67	32.11	6.1	1.19	5.2	0.87	4.94	0.95	2.82	0.46	2.95	0.47	26.64	199.4	153.5	45.3
Max.	189.63	337.69	38.51	125.47	20.55	2.8	17.47	2.55	12.96	2.41	6.81	1.04	6.53	1.04	71.5	799.8	704.2	122.3
Mean	32.53	62.8	7.86	28.99	5.44	1.08	4.65	0.78	4.42	0.86	2.51	0.41	2.62	0.42	23.79	179.1	138.7	40.5
CGB (P50)	32.65	63.72	7.61	28.22	5.31	1.12	4.65	0.75	4.47	0.86	2.48	0.41	2.58	0.42	23.7	179.93	139.28	40.34

region.

Notation: Sample medium, stream sediments; grain size, -100 mesh; number of samples = 1067; P = percentile (P50 = median); Min. = minimum; Max. = maximum.

contents in soils formed by the weathering of biotite granite, monzogranite, and rhyolite are basically unchanged (Table 3).

Overall, the REE content in soils is primarily determined by the parent rocks. The chondrite normalized REE patterns of soils are similar to that of the parent rocks, indicating that in the semi-arid grassland region, basically, no fractionation occurs between heavy and light REE after the parent weathering, suggesting that the REE distribution pattern has a good inheritance.

During chemical weathering, cerium (Ce) tends to behave differently from other REE. Cerium in the oxidizing environment occurs as Ce^{4+} and highly insoluble as CeO_2 whereas the other REEs maintain their 3⁺ionic states and are leached by circulating water (Mihajlovic and Rinklebe, 2018). The absence of Ce anomaly in the soils of the study area indicates that the area is dominated by the physical weathering process, and the chemical weathering process is relatively weak.

Hence, it is possible to determine the sources by the REE distribution pattern in sediments.

4.4. REE distribution in soil profile

As shown in Fig. 10, the weathered profile shows a vertical variation in which the REE content decreases from the surface (0–10 cm) to the middle horizon, but increases near the bedrock. The REE content variation with depth is consistent for all fractions. However, the CaO content variation with depth is quite different from REE. The CaO contents in the surface and near the bedrock are very low, but the CaO content in the middle horizon (10–30 cm) increases tremendously with a pH of 9.1 (Fig. 11), indicating the existence of caliche in the middle horizon.

Generally, the influencing factors on REE content include parent material, the content of clay, carbonate (CO_3) , total organic carbon (TOC) and sesquioxides (Brunsmann et al., 2001; Canovas et al., 2018; Ling et al., 2015; Mihajlovic and Rinklebe, 2018). The chemical/physical soil properties are partly influenced by pedogenic processes which also lead to the depletion or enrichment of REE in parts of the soil profiles since REE are involved in the processes. In this study, the REE in the investigated soil profile shows little relations with TOC, Fe, and Mn oxides. The decrease of REE in the middle horizon is mainly influenced by the existence of a caliche.

4.5. REE dispersion pattern along the stream

Over a long mining history of the main orebody of Bayan Obo, deposition of materials has caused REE contamination in the surrounding area. Considering that the prevailing wind direction in this area is northwest, to minimize the potential impact of REE contamination on the results of our study, we selected the northwestward streams to the west orebody for investigation (Fig. 1). To verify whether this district has been contaminated by dust fall, we collected three soil samples from sites about 500 m, 700 m, and 900 m from the west orebody (red spots in Fig. 2). The REE contents are 189 μ g/g, 209 μ g/g, and 192 μ g/g, respectively, which approximate the background value of 170.8 μ g/g for the study area (see above). Hence, it can be assumed that the study area was not contaminated at the time of sampling.

Fig. 12 shows that the total REE content in the bulk grain sample rapidly decreases with the migration distance, decreasing to the background value at around 3.0 km from the orebody. As mentioned above, the 20–40 mesh and 40–80 mesh fractions contain relatively high quartz and feldspar contents. With increasing distance from the orebody, the total REE content sharply decreases, decreasing to the background value at around 2.5 km from the orebody. The REE content in the fine fractions (80–120 mesh, < 120 mesh) gradually decreases along the river, but is still relatively high at 7 km and has not decreased to the background value. This result indicates that REEs migrate with coarse particles over short distances and can transport over long distances in the form of fine particles. This finding is highly significant to REE geochemical mapping in that REE anomalies cannot be effectively identified at 1:1,000,000 or global-scale geochemical mapping unless fine-grained samples are collected.

Chondrite-normalized (Sun and McDonough, 1989) REE patterns of upstream and downstream samples (Fig. 12) show that the REE content in upstream sediment is higher than that in downstream sediment, and higher LREE/HREE ratios and significant Eu negative anomaly occur in the chondrite-normalized REE patterns of upstream sediment, indicating distinct provenances of upstream and downstream samples. The REE patterns of different fractions of upstream samples are essentially identical, suggesting that all materials of the upstream sample originate from the same source.

The downstream samples contain a relatively low total REE content for the medium and coarse fractions and a relatively high total REE content for the fine fractions. The fine-grained samples show a considerable LREE/HREE ratio and an obvious negative Eu anomaly,





Fig. 9. Chondrite-normalized (Sun and McDonough, 1989) REE patterns of rocks and in situ weathered soils.

Table 3

Contents of REEs ($\mu g/g$) in parent rocks and in-situ soils.

Sample no.	Sample type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
	Biotite granite	48	84	9.3	32	4.7	1.2	3.9	0.6	3.3	0.6	1.8	0.3	1.9	0.3	17
C04-1S1	Soil in-situ	30	59	6.8	26	4.6	1.1	3.9	0.6	3.4	0.6	1.9	0.3	1.9	0.3	18
C04-1S	Soil in-situ	26	52	5.7	22	3.8	1	3.4	0.5	2.9	0.6	1.7	0.3	1.8	0.3	16
BOR06	Monzogranite	49	102	11.7	41	7.3	1.5	6.4	1	5.9	1.1	3.5	0.6	3.8	0.6	33
BOR06S	Soil in-situ	44	83	9.6	35	5.5	1.2	4.6	0.7	4.1	0.8	2.4	0.4	2.4	0.4	22
BOR05	Rhyolite	57	100	12.4	45	7.7	1	7.1	1.3	7.1	1.4	4.1	0.6	4.1	0.6	38
BOR05S	Soil in-situ	75	140	15.3	54	7.9	1.5	6.5	1	5.1	1	2.9	0.5	3	0.5	28
E04-1R	Sandstone	6	34	1.8	7	2	0.1	2	0.5	3.6	0.8	3	0.6	4.4	0.8	22
E04-1S	Soil in-situ	13	27	3.7	15	4.3	0.3	4.1	0.8	5.3	1.1	3.5	0.6	4.4	0.8	35
BOR08	Feldspathic quartz	23	43	5.4	20	3.5	0.9	3.3	0.6	3.1	0.6	1.8	0.3	1.9	0.3	16
	Sandstone															
BOR08S	Soil in-situ	43	82	9.6	36	6.5	1.3	5.5	0.9	5	1	2.9	0.4	3	0.5	28
BOR07	Dolomite	16	33	4.2	16	2.7	0.6	2.3	0.4	2.1	0.4	1.2	0.2	1.1	0.2	12
BOR07S	Soil in-situ	43	85	9.9	37	6	1.2	5.2	0.8	4.3	0.8	2.5	0.4	2.5	0.4	24
BOR10	Biotite-plagioclase	16	31	4	15	3	0.7	2.9	0.5	2.8	0.6	1.7	0.3	1.8	0.3	15
	Hornblende schist															
BOR10S	Soil in-situ	42	76	9.1	35	6	1.3	5.3	0.9	4.7	0.9	2.7	0.4	2.8	0.4	25
B0R11	Slate	76	142	16.2	57	10	1.9	8.2	1.4	7.7	1.5	4.2	0.7	4.3	0.8	38
BOR11S	Soil in-situ	53	100	11.9	45	7.7	1.5	6.6	1.1	5.6	1.1	3.4	0.5	3.4	0.6	32



Fig. 10. Depth profile of the REE content for different fractions (A, bulk size; B, 4–20 mesh; C, 20–40 mesh; D, 40–80 mesh; E, 80–120 mesh; F, < 120 mesh).

whereas the coarse-grained samples have a relatively low LREE/HREE ratio and obscure negative Eu anomaly. This signifies different material sources for the downstream coarse-grained samples and fine-grained samples. A comparison with the REE distribution pattern of the upstream samples reveals that the downstream fine-grained samples share

the same REE distribution pattern with the upstream samples (Fig. 13). This further confirms that the downstream fine-grained materials were transported over long distances from upstream, resulting in a high REE content in these materials. The downstream medium- and coarse-grained materials are mainly products of in-situ weathering. Therefore,



Fig. 11. Depth profile of the CaO content for different fractions (A, bulk size; B, 4–20 mesh; C, 20–40 mesh; D, 40–80 mesh; E, 80–120 mesh; F, < 120 mesh).

physical weathering is the main weathering process in this area. REEs in the surficial environment migrate via mechanical means and REEs can migrate with fine-grained particles over long distances (7 km or longer). Coarse-grained samples, in contrast, typically remained in situ.

5. Conclusions

In the Bayan Obo region, slate and acidic rocks contain higher REE contents than quartz, sandstone, or limestone. Within the Bayan Obo Group, REE content in the Bilute, Jianshan, and Dulahala Formation slates are far higher than those in the continental crust or the continental crust of the NCC. These surrounding rocks might have provided sufficient REE sources to form this huge REE deposit in the Bayan Obo region. The total REE content of stream sediments in the Bayan Obo region ranges from 46.9 to 799.8 μ g/g, with a median of 170.8 μ g/g. Two large-scale REE anomalies were discovered to the west of the Bayan Obo region.

Although the main orebody of the Bayan Obo deposit has been mined for a long time, the northwestern area of the west orebody has

remained uncontaminated. The REE content in soil is primarily determined by the parent rock. The chondrite-normalized REE patterns of soils are similar to those of the parent rocks, indicating that in semi-arid grassland region, no fractionation occurs between heavy and light REEs after the parent rock weathers. Hence, the sources of the REE can be determined through the REE distribution pattern in sediments.

Across the soil weathering profile, REEs are typically abundant in the surface and deep layers. In the middle horizon, the REE content is usually lower owing to the existence of caliche in the middle horizon.

REEs primarily migrate along streams via mechanical means in semi-arid grasslands in Inner Mongolia. REEs can migrate with finegrained samples over long distances (7 km or longer), whereas coarsegrained samples typically remain in situ. Affected by aeolian sand, the REE content is relatively low in the 40–80 mesh fraction.

Our findings define the natural background and distribution of REEs to distinguish their natural variations related to geology from mineralization and contamination and provide useful information for lowdensity geochemical mapping of REEs.



Fig. 12. Total REE content along the stream for different fractions (the black dotted line represents the REE background value of the area, 170.8 µg/g).



Fig. 13. Chondrite-normalized (Sun and McDonough, 1989) REE patterns of upstream and downstream samples.

CRediT authorship contribution statement

Jian Zhou: Conceptualization, Methodology, Software, validation, Data curation, Writing - Original draft preparation, Writing review & editing. Xueqiu Wang: Conceptualization, Methodology, Software, Data curation, Writing- Original draft preparation, Writing - review & editing. Lanshi Nie: Conceptualization, Methodology, validation, Writing - review & editing.Jennifer McKinley: Writing - Original draft preparation, validation, Writing review & editing. Hanliang Liu: Conceptualization, Methodology, Software, validation, Data curation validation, Writing - review & editing. Bimin Zhang: Conceptualization, Methodology, Software, validation, Data curation validation, Writing - review & editing. Data curation validation, Writing - review & editing. Data curation validation, Writing - review & editing. Zhixuan Han: Conceptualization, Methodology, Software, validation, Data curation validation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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