

# Analysis of Contents and Distribution Patterns of Rare Earth Elements in the Surface Sediments of the South Mid-Atlantic Ridge



LI Jing-Xi<sup>1,2,\*</sup>, ZHU Zhi-Wei<sup>1</sup>, YIN Xiao-Fei<sup>1</sup>, HAN Bin<sup>1</sup>, ZHENG Li<sup>1</sup>, WANG Jiang-Tao<sup>2</sup>, WANG Xiao-Ru<sup>1</sup>

<sup>1</sup> Marine Ecology Research Center, First Institute of Oceanography of State Oceanic Administration, Qingdao, Shandong 266061, China

<sup>2</sup> College of Chemistry and Chemical Engineering of Ocean University of China, Qingdao, Shandong, 266100, China

**Abstract:** A microwave digestion system was employed to digest sediment samples from 16 stations in the South Mid-Atlantic Ridge with HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HF as the digestion reagent. Rare earth elements (REEs) in the sediments were determined through inductively coupled plasma-mass spectrometry (ICP-MS), and the REE distribution characteristics were studied. The microwave digestion-ICP-MS method was used to determine the REEs with significant linear relationships ( $r = 0.9997-1.0000$ ) for each element. The detection limit was at ng L<sup>-1</sup> level, with relative standard deviation (RSD,  $n = 3$ ) of less than 3% and the relative error within 6%. Moreover, the total amount of REEs ( $\sum$ REEs) in the sediment samples from the 16 stations ranged from 37.25 to 134.8  $\mu\text{g g}^{-1}$ , the ratio range of the light/heavy REEs (LREEs/HREEs) was 0.61–1.70, the average value was 1.27, and the enrichment light rare earth elements in sediments was obvious. The REE distribution patterns in each station were similar, with obvious fractionation between the LREEs and HREEs. The REE distribution patterns in the sediments from different sources were also similar, but those between the terrestrial and marine sediments exhibited slight differences. The  $\delta\text{Eu}$  and  $\delta\text{Ce}$  in the sediments had negative anomalies, which showed that the REEs in the sediments originated from seawater. The content and distribution of the REEs in the South Atlantic were initially investigated in this study to provide data and technical support for the further study of REE distributions in the Atlantic region.

**Key Words:** Southern Atlantic; Rare earth element; Inductively coupled plasma-mass spectrometry; Sediments

## 1 Introduction

Various parameters, such as the abundance and distribution pattern of rare earth elements (REEs) in submarine sediments, are significant to examine the formation conditions and character of the provenance of submarine sediments<sup>[1–4]</sup>. REEs normally migrate as collectively during the chemical reactions of the Earth, but different REEs have minor distinctions in nature. Fractionation may occur among different REEs because of the changes in external conditions. Thus, REEs are significant indicators of geochemistry<sup>[5–8]</sup>. The amounts and distribution patterns of REEs can be used to determine the type of geological bodies, and the distinct characteristics of

elements reveal the migration, enrichment, and environmental change during the evolution of geological formation. In the studies on submarine sediments, REEs reflect the overall characteristics and differences various submarine sediments, as well as the properties and evolution of water bodies on geochemistry in different historical periods, oceanic clay origins, and geochemistry records of volcanisms.

The REE distribution characteristics in the submarine sediments of the coastal waters of China were comprehensively studied. Lan *et al.*<sup>[9]</sup> analyzed the REE distribution characteristics in the columnar sediments of the central South Yellow Sea and performed tracer analysis on the paleoclimate of the provenance of Yangtze River and Yellow

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\*Corresponding author. Email: jxli@fio.org.cn

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River. Zhuang *et al.*<sup>[10]</sup> indicated that particle size regulates the REE distributions in the surface sediments of the subaqueous Changjiang River Delta. Wang *et al.*<sup>[11]</sup> and Liu *et al.*<sup>[12]</sup> introduced the REE migration and transportation modes, as well as the phase distributions of the Yangtze River estuary. Most studies on REEs in marine environments focused on estuaries and greater coastal areas, but research on REEs in oceans remained relatively insufficient.

Sediment samples from the South Mid-Atlantic Ridge area (11.8852° W00–14.5193° W, 13.3552° S–19.4052° S) were collected in this study, and the REE contents in the sediments were measured through inductively coupled plasma-mass spectrometry (ICP-MS) after pretreatment with a microwave digestion system. In this study, an accurate and reliable test method was employed with a low detection limit. Moreover, the REEs content range and distribution patterns in the South Atlantic sediments were studied, and the  $\delta\text{Eu}$  and  $\delta\text{Ce}$  values were calculated. In addition, the REE origins were studied. This study provided a necessary basis for further research on environmental issues in the Atlantic Ocean region.

## 2 Experimental

### 2.1 Instruments and reagents

The equipments included a inductively coupled plasma mass spectrometry (Agilent ICP-MS 7500a), a Milli-Q ultra pure water treatment system (Millipore Co.18.2 M $\Omega$  cm), a microwave digestion system (CEM), a freeze dryer (Germany Christ Alpha 1-4 LSC); and an electronic analytical balance (Mettler-Toledo AL104).

The reagents included 10 mg L<sup>-1</sup> standard solution of rare earth elements (SPEX CertiPrep Co.), 65% nitric acid (Merck) and 30% hydrogen peroxide (Merck) which were used for DSP samples digestion, liquid argon (> 99.999%), 10 mg L<sup>-1</sup> tuning solution including Li, Co, Y, Tl and Ce, 10 mg L<sup>-1</sup> internal standard solution of Re (SPEX CertiPrep Co.) diluted to 100  $\mu\text{g L}^{-1}$  with 5% HNO<sub>3</sub> before being used. The Yellow Sea marine sediment composition analysis standard material (GBW07333 China) and the Milli-Q ultra pure deionized (DI) water (Millipore, USA) were used throughout the experiment.

### 2.2 ICP-MS working parameters

A tuning solution was used to tune the ICP-MS to obtain the best analysis requirements for high sensitivity and

resolution, low double charge and oxide. The radio frequency power was 1350 W. The flow rates were 15.0 L min<sup>-1</sup> for the plasma gas, 1.18 L min<sup>-1</sup> for the carrier gas, and 1.0 L min<sup>-1</sup> for the auxiliary gas. Moreover, the sampling depth was 6.5 mm, the spray chamber temperature was set at 2.0 °C, the sample uptake rate was 1.00 mL min<sup>-1</sup>, the acquisition mode was the quantity, the integration time was 0.5 s, the dwell time was 30 ms, and the number of replicates was 3.

### 2.3 Sample collection

The surface sediment samples were collected from 16 stations in the South Mid-Atlantic Ridge area during the 26th Oceanic Cruises (2013) using sediment traps. The samples were then frozen immediately under -20 °C. The sediment samples were freeze-dried, ground, and sifted through an 80 mesh porous sieve. The sampling station details are shown in Table 1.

### 2.4 Sample preparation and measurement

First, 0.20 g of sediment sample was predigested at room temperature using 6 mL HNO<sub>3</sub>-2 mL H<sub>2</sub>O<sub>2</sub>-1 mL HF in a Teflon (PTFE) tank for 2 h, and then a microwave digestion system was used to digest the sample according to the details in Table 2. Second, the solution was weighted with 25 g ultrapure water for measurement after digestion. Third, a series of rare earth multi-element mixed standard solutions (0.0, 1.0, 2.0, 5.0, 10.0 and 20.0  $\mu\text{g L}^{-1}$ ) were prepared and then added to Re as internal standard online. A standard curve

Table 1 Information of sampling stations

Sample No.	Longitude	Latitude	Depth (m)
S1	11.8852°W	19.4052°S	2401
S2	11.9303°W	19.2607°S	2559
S3	11.9997°W	19.3203°S	2602
S4	12.7046°W	18.4878°S	2152
S5	12.8535°W	18.0387°S	3312
S6	12.8541°W	18.4827°S	3223
S7	13.3434°W	15.1604°S	3032
S8	13.3461°W	15.1643°S	2854
S9	13.3562°W	15.1661°S	2730
S10	14.3112°W	13.3552°S	3142
S11	14.3764°W	14.0457°S	2796
S12	14.5172°W	13.5933°S	3051
S13	14.5186°W	13.5956°S	3059
S14	14.5191°W	13.5943°S	3125
S15	14.5192°W	13.5935°S	3142
S16	14.5193°W	13.5896°S	3203

Table 2 Working parameters of microwave digestion

Stage	Power (W)	Temperature (°C)	Ramp time (min)	Hold time (min)
1	1500	100	3:00	3:00
2	1500	150	7:00	3:00
3	1500	170	5:00	3:00
4	1500	190	5:00	10:00

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