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RESEARCH PAPER

Study on Ecological and Chemical Properties of Rare Earth Elements in Tropical Marine Organisms

LI Jing-Xi[1], ZHENG Li[1,2], SUN Cheng-Jun[1,*], JIANG Feng-Hua, YIN Xiao-Fei[1], CHEN Jun-Hui[1], HAN Bin[1], WANG Xiao-Ru[1]

[1] Marine Ecology Research Center,First Institute of Oceanography of State Oceanic Administration, Qingdao 266061,China
[2] Laboratory of Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, China

Abstract: A total of 30 kinds of fish samples, 5 kinds of shellfish samples and 4 kinds of crustacean samples from the Nansha sea area in China were digested using a microwave digestion system with HNO_3-H_2O_2 as the digestion reagent. Then, the contents (ICP-MS determination) and ecological chemical characteristics of rare earth elements (REEs) were studied. The results showed that the method of microwave digestion-ICP-MS for the determination of rare earth elements was perfect, and the linear relationship for each element was good with $r \geq 0.9997$. The detection limit reached ng L^{-1} level with a relative standard deviation (RSD, $n = 3$) of less than 5.0%. The recovery of REEs was between 91.5% and 106.7%. The total amount of REEs in fishes, shellfishes, and crustaceans were (5.0–34.8) μg kg^{-1}, (30.4–1481) μg kg^{-1}, and (103–863) μg kg^{-1}, individually. The order of the enrichment average contents of the REEs in the three species was crustacean>shellfish>fish. The 14 kinds of REE contents in fish/shellfish/crustacean showed a significantly positive correlation ($r > 0.80$). The contents of light REEs (from La to Eu) were higher than those of heavy REEs (from Gd to Lu). The light and heavy REEs demonstrated obvious fractionation, and the REE distribution pattern in fish/shellfish/crustacean was consistent with the negative anomaly of Gd. The δEu values had negative anomalies, which were similar to the δEu values in the corresponding area sediment, and δCe values showed positive anomalies, which showed that Ce followed a different oxidation and reduction process in the organism and sediment deposition. At the same time, the enrichment relationship of REEs in sediment and organism was also studied. In this study, the content and distribution of REEs in the tropical marine fish/shellfish/shellfish were analyzed, which could provide basic data for the study of the level, migration, and accumulation of REEs in the environment of South China Sea.

Key Words: Tropical organisms; Rare earth element; Rare earth distribution pattern; Inductively coupled plasma mass spectrometry

1 Introduction

Rare earth elements (REEs) are important mineral elements, which consist of the La-series elements divided into light REEs (LREEs) (Sc, Y, La, Ce, Pr, Nd, Pm, Sm and Eu) and heavy REEs (HREEs) (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). REEs in geochemical processes always migrate as a whole; however, the properties of different REEs still show slight differences[1–3]. Low concentrations of REEs have significant anti-cancer and anti-mutagenic effects, whereas high concentrations would cause brain and nerve accumulation toxicity hazard, etc[4,5]. In recent years, with the extensive use of REEs in the fields of agriculture, medicine and health, industry, high-tech industries, etc., REEs inevitably entered the biosphere through a variety of ways and eventually entered the human body. Therefore, the studies on the effect and mechanism of REEs on the organism are of great significance[6–10].

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*Corresponding author. Email: Csun@fio.org.cn
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At present, the studies on REEs in the marine environment are mainly focused on the establishment of methods for the determination of REEs in minerals, marine sediments, estuarine waters, and their geochemical characteristics[11–13]. Zhuang *et al*[14] indicated that particle size regulated the REEs distributions at the surface sediments of the subaqueous Changjiang River Delta. Chen *et al*[11] established an ICP-MS method for the determination of trace REEs in soil and sediment. Lan *et al*[15] analyzed the REEs 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 River. The REEs migration and transportation modes were introduced[16,17], as well as the phase distributions of the Yangtze River estuary. Recently, some studies analyzed the REEs in organisms, for instance, Wang *et al*[18] analyzed the differentiation phenomenon of REEs in tea; Chen *et al*[19] studied the concentrations of REEs in three types of shellfish. However, the contents of REEs in marine organisms are relatively rare. REEs have a significant "hormesis effect" on marine organisms[20,21]. For example, REEs have middle and low toxicity in algae but stimulate algal growth under low concentrations[22]. With the research progress of REEs in biology, the effects of REEs in plant enrichment and humans via the food chain can be easily studied. However, the cause and mechanism of the distribution pattern in organisms and water is unclear, and such matters are important for future research on the role of REEs in the environmental biogeochemistry cycle.

In this study, to study the enrichment, distribution patterns, and biological effects of REEs in large marine organisms, the tropical fishes, shellfishes and crustaceans were collected from the Nansha sea area in China. The concentration and distribution pattern of 14 types of REEs were measured by microwave digestion and ICP-MS. Thereafter, the REEs distribution correlation among organisms was investigated. δEu and δCe were also calculated. The REE correlation of organism enrichment and sediment deposition was analyzed. This study provided the necessary basis for further research on the distribution characteristics and biological availability of REEs in the Nansha Sea in China.

2 Experimental

2.1 Instruments and reagents

The samples were digested by a MARS microwave digestion instrument (America, CEM Co.). Mass spectrometric analysis was performed on an inductively coupled plasma mass spectrometer (America, Agilent 7500a). Vacuum freezing dryer (America, Labconco Co.) and AL104 electronic analytical balance (Mettler-Toledo) were also used in the experiment. Otherwise, pure water produced by a Milli-Qultra pure water treatment system (Milipore Co., 18.2 MΩ cm) was used throughout the experiment.

Concentrated nitric acid (GR) and H_2O_2 (GR) were purchased from Merck, Germany. Standard solution of rare earth elements (10 mg L^{-1}) was obtained from SPEX CertiPrep Co., America. Internal standard solution of Re (10 mg L^{-1}) was from SPEX CertiPrep Co., America. Liquid argon (99.999%) and standard substance for trace elements in mussels (BCR-668) were also used in the experiment.

2.2 Instrument working parameters

A tuning solution was used to tune the ICP-MS to obtain the best analysis requirements for sensitivity, double charge, oxide, and resolution. The working parameters of ICP-MS are shown in Table 1.

2.3 Sample collection

Fish, shellfish and crustacean samples were obtained from the Nansha sea area of China in summer of 2015. Fishes mainly included *Ostracion meleagris, Cephalopholis argus, Balistapus undulates, Cephalopholis urodelus, Gymnothorax moringa, Kyphosuslembus, Parupeneus multifasciatus, Parupeneus pleurostigma, Melichthys vidua*, *Pervagor melanocephalus*, *Cheilinus fasciatus*, *Cheilinusrhodochrous*, *Cephalopholis sonnerati*, *Odonus niger*, *Cypselurus katoptron*, *Heteropriaccmthuscruentatus*, *Gnathodentex aureolineatus*, *Paraluteres prionurus Bleeker*, *Myripristiscf.kuntee*, *Epinephelus hexagonatus*, *Coris gaimard*, *Scarus forsteri*, *Diodonhystrix*, *Parupeneustrifasciatus*, *Epinephelus,groupers*, *Lutjanus kasmira*, *Cephalopholis urodelus*, *CommonAngel fish*, *Ctenochaetus striatus* and *Halassomaquinquevittatus.* Shellfishes mainly contained *Eustrombusgigas*, *Trochus niloticus*, *Linnaeus*, *Harpago chiragra* and *Tridacna squamosa*. Crustaceans mainly included *Dromia dehaani*, *Paguridae*, *Podophthalmus vigil* and *Carpilius convexus*. The organism samples were frozen immediately and taken to laboratory under –20 °C after being identified. All samples were

Table 1 Working parameters of ICP-MS

Item	Parameters
RF power	1350 W
Sampling depth	6.3 mm
Plasma gas	16.0 L min^{-1}
Auxiliary gas	1.0 L min^{-1}
Carrier gas	1.15 L min^{-1}
Aperture of sampler (Ni)	1.0 mm
Aperture of skimmer(Ni)	0.8 mm
Sample uptake rate	1.0 mL min^{-1}
Acquisition mode	Quantity
Scan mode	Jump
Dwell time	30 ms
No. of replicates	3
Integration time	0.1000 s