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Journal of Alloys and Compounds 408–412 (2006) 985–988

Journal of ALLOYS AND COMPOUNDS

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Determination of rare earth elements in seawater by ICP-MS after preconcentration with a chelating resin-packed minicolumn

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Received 22 July 2004; received in revised form 2 December 2004; accepted 2 December 2004
Available online 24 June 2005

Abstract

Rare earth elements (REEs) in seawater were preconcentrated 20-fold (from 50 to 2.5 ml) by a chelating resin-packed minicolumn device and determined by inductively coupled plasma mass spectrometry (ICP-MS). The recoveries for REEs were in the range from 90% for Eu and Dy to 98% for Yb, and their standard deviations were less than 4%. The lower detection limits for REEs ranged from 0.06 ng l^{-1} for Lu to 0.5 ng l^{-1} for Sm. The analytical results for REEs in seawater reference materials (NASS-5, CASS-3, and CASS-4), the Take Island coastal seawater, and the Ise Bay coastal seawater were evaluated as the REE distribution patterns with shale-normalization and deep seawater-normalization. Slight relative enrichments of heavy REEs were observed in the Take Island coastal seawater and the Ise Bay coastal seawater, which might be attributed to the input from the river flows containing more dissolved heavy REEs. In addition, positive anomalies of Sm were found in the normalized REE distribution patterns for NASS-5, CASS-3, and CASS-4, which would be attributed to the contamination in the preparation process of reference materials by NRC.

Keywords: Rare earth elements; Seawater; ICP-MS; Chelating resin-packed minicolumn

1. Introduction

Rare earth elements (REEs) have attracted much attention in the researches on marine geochemistry, where they serve as tracers of water masses and ocean circulation [1–3] and also as a valuable probe for investigating the scavenging processes of particulate matter [4–6]. The development of analytical instruments, especially inductively coupled plasma mass spectrometry (ICP-MS), benefited the determination of REEs greatly by providing excellent multi-element detection capability with high sensitivity and wide linear dynamic range, which allows direct determination of trace metals at ppt (ng l^{-1}) levels [7,8]. However, the direct ICP-MS determination of REEs in seawater is still difficult because of the extremely low concentrations of REEs and the high dissolved salt contents in seawater. Especially, the high salt contents as matrix elements in seawater cause instrumental drift, spectral interferences, signal suppression, and cloggings of the sample introduction system of the instrument. Therefore, solvent extraction [3,9], co-precipitation [10], and chelating resin adsorption [11,12] have been developed as pretreatment techniques to eliminate matrix elements as well as to preconcentrate trace metals in seawater for their determination by ICP-MS.

In the present research, a simple but practical chelating resin-packed minicolumn was constructed as the laboratory-made device and applied to the preconcentration of REEs in seawater. The concentrations of REEs in the Take Island coastal seawater, the Ise Bay coastal seawater, and seawater reference materials (NASS-5, CASS-3, and CASS-4) from the National Research Council (NRC) of Canada were determined by ICP-MS. The results were compared with one another through the REE distribution patterns normalized

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doi:10.1016/j.jallcom.2004.12.092

to the concentrations of REEs in shale and deep seawater, respectively.

2. Samples and method

2.1. Seawater samples

Coastal seawater sample from the Take Island (Gamagori, Aichi prefecture, Japan) was collected near shore of the island, and that from the Ise Bay was collected at about 1 km off-shore near the Nagoya Port (Nagoya, Aichi prefecture, Japan). The samples were filtered with a membrane filter (pore size 0.45 μm) immediately after sampling, and then acidified to pH 1 with concentrated nitric acid. The coastal seawater samples were preserved in the polypropylene tanks, which were soaked in 6 M nitric acid for more than a week and rinsed with pure water just before use. Seawater reference materials (NASS-5, CASS-3, and CASS-4) were purchased from NRC (Canada).

2.2. Procedure for preconcentration

A chelating resin-packed minicolumn developed by the present authors [13] was applied to the preconcentration of REEs in seawater samples. The minicolumn was constructed as a combination of two commercially available syringe filters and 0.40 g of Chelex 100 resin (Bio-Rad Laboratories) in wet weight was packed into the space between the filter tubes. The procedure for preconcentration of trace metals in seawater was as follows.

First, 5 ml of 1 M ammonium acetate buffer (pH 6.0) was passed through the minicolumn for conditioning; and then 50 ml of seawater sample (adjusted to pH 6.0) was loaded into the minicolumn at the flow rate of 3 ml min^{-1} by using a 50 ml syringe. Second, 8 ml of 1 M ammonium acetate buffer (pH 6.0) and 5 ml of pure water were successively injected at the flow rate of 2 ml min^{-1} for rinsing to minimize the amounts of matrix elements (Mg^{2+} and Ca^{2+}) adsorbed on the resin. Finally, trace metals adsorbed on the chelating resin were eluted with 2.25 ml of 2 M HNO_3 and collected in a 5 ml test tube. After 0.25 ml of internal standard solution (Ge, In, Re, Tl 100 μg l^{-1} each) was added to the above-stated eluate to correct matrix effects, the final solution was subjected to the determination of trace metals by ICP-MS (Agilent HP4500, Yokogawa, Tokyo, Japan). For the recovery test, REEs (0.1 μg l^{-1} each) were spiked in the seawater sample, and the same preconcentration as described above was performed.

3. Results and discussion

3.1. Analytical results for REEs in seawater samples

The recoveries, blank values and analytical detection limits for REEs are shown in Table 1, as the analytical figures of merit of the present method. In the present experiment, the polyatomic interferences with REEs were corrected according to the interference correction coefficient method reported by Yabutani et al. [11]. The interference ratios (the ratios of the apparent concentrations due to interfering element to the concentrations of analyte elements) for all REEs were less than 5%. Thus, the results for REEs in the present research were not subject to noticeable correction of polyatomic interferences.

Table 1
Analytical figures of merit for REEs

Element	m/z	Recovery[a] (%)	Blank (ng l^{-1})	ADL[b] (ng l^{-1})
La	139	96 ± 3	0.4	0.1
Ce	140	94 ± 3	<0.4	0.1
Pr	141	93 ± 3	n.d.	0.07
Nd	143	93 ± 4	n.d.	0.3
Sm	147	95 ± 3	n.d.	0.5
Eu	153	90 ± 2	n.d.	0.1
Gd	157	91 ± 4	n.d.	0.4
Tb	159	92 ± 2	n.d.	0.08
Dy	163	90 ± 2	n.d.	0.3
Ho	165	93 ± 3	n.d.	0.07
Er	166	91 ± 4	n.d.	0.2
Tm	169	91 ± 1	n.d.	0.08
Yb	172	98 ± 2	n.d.	0.3
Lu	175	91 ± 1	n.d.	0.06

n.d.: not detected.

[a] Mean value ± standard deviation, $n = 3$.

[b] Analytical detection limit, calculated from instrumental detection limits, taking into account the concentration factor (20) and recovery values.

REEs in NASS-5, CASS-3, CASS-4, the Take Island coastal seawater and the Ise Bay coastal seawater were determined in the present experiment. The results are summarized in Table 2. All the concentrations of REEs in Table 2 were corrected with the recovery values listed in Table 1.

3.2. Shale-normalized REE distribution patterns in the seawaters

The shale-normalized REE distribution patterns, which are shown as the relative concentrations of REEs normalized to their concentrations in shale and plotted against atomic number, are often examined in order to evaluate internal consistency of the REEs data for seawaters [11]. The REE distribution patterns for seawaters examined are shown in Fig. 1, where the concentrations of REEs were normalized to those in post-Archean average Australian shale (PAAS) [14]. It is seen in Fig. 1 that the REE distribution patterns show smooth curves in general, with slight enrichment of heavy REEs and clear negative anomalies of Ce in all seawater samples. These results are consistent with those previously reported REE distribution patterns of seawaters [11]. However, the Take Island coastal seawater and the Ise Bay coastal seawater showed relatively large enrichment of heavy REEs than those in seawater reference materials. This may be explained by the input of dissolved REEs from river water fluxes, which generally

Table 2
Analytical results for REEs in seawater samples

Element	*m*/*z*	Concentration[a] (ng l^{-1})				
		NASS-5	CASS-3	CASS-4	The Ise Bay	The Take Island
La	139	11.1 ± 0.5	13.6 ± 0.4	10.0 ± 0.4	12.3 ± 0.9	5.96 ± 0.27
Ce	140	4.9 ± 0.3	6.7 ± 0.4	6.1 ± 0.3	10.2 ± 0.6	3.9 ± 0.2
Pr	141	1.9 ± 0.1	1.9 ± 0.1	1.42 ± 0.04	2.05 ± 0.05	1.09 ± 0.07
Nd	143	6.8 ± 0.5	7.5 ± 0.4	5.5 ± 0.5	6.4 ± 0.6	4.3 ± 0.1
Sm	147	4.0 ± 0.3	7.1 ± 0.6	5.5 ± 0.5	0.9 ± 0.1	1.5 ± 0.1
Eu	153	0.35 ± 0.01	0.28 ± 0.04	0.19 ± 0.03	0.46 ± 0.06	0.43 ± 0.01
Gd	157	2.1 ± 0.1	1.5 ± 0.2	1.4 ± 0.2	3.5 ± 0.4	2.4 ± 0.1
Tb	159	0.22 ± 0.01	0.30 ± 0.01	0.17 ± 0.03	0.40 ± 0.05	0.25 ± 0.03
Dy	163	1.8 ± 0.1	1.9 ± 0.2	1.5 ± 0.2	2.97 ± 0.09	2.9 ± 0.3
Ho	165	0.44 ± 0.02	0.47 ± 0.02	0.35 ± 0.03	0.73 ± 0.02	0.60 ± 0.05
Er	166	1.3 ± 0.1	1.31 ± 0.05	1.1 ± 0.1	3.0 ± 0.2	2.0 ± 0.2
Tm	169	0.19 ± 0.02	0.20 ± 0.04	0.20 ± 0.05	0.51 ± 0.05	0.35 ± 0.04
Yb	172	1.3 ± 0.1	1.2 ± 0.2	1.2 ± 0.2	3.9 ± 0.2	2.7 ± 0.3
Lu	175	0.22 ± 0.02	0.25 ± 0.02	0.16 ± 0.03	0.9 ± 0.1	0.54 ± 0.07

[a] Mean ± standard deviation, $n = 5$.

contain the higher concentrations of heavy REEs [15,16]. On the other hand, in all seawater reference materials (NASS-5, CASS-4, and CASS-3), higher concentrations of Sm were observed. As has been reported [11], contamination of Sm was seemingly caused in preparation process of those reference materials. Besides, the results for the Take Island and Ise Bay coastal seawaters did not show the high concentration of Sm like those in reference materials. It may, thus, be reasonable to consider that Sm in seawater reference materials was contaminated during preparation of these reference materials.

3.3. Deep seawater-normalized REE distribution patterns in the seawaters

Nozaki et al. proposed North Pacific deep water (NPDW)-normalization as an alternative to generally used shale-normalization for detailed arguments concerning fractionation between different water masses [17,18]. The NPDW-normalization could get rid of the similarities among seawater samples, for example the slight enrichment of heavy REEs in shale-normalization, so that the differences of water masses could be better observed and evaluated. Thus, NPDW-normalization was applied to the analytical results obtained in the present experiment, where the concentrations of REEs were normalized to the average values for three deep waters at about 2500 m depths in the western North Pacific Ocean, as Nozaki et al. reported [17]. The results are shown in Fig. 2. It is seen that all seawaters examined showed flat curves with slight enrichment of heavy REEs in the Take Island coastal seawater and the Ise Bay coastal seawater as well as Sm contaminations in seawater reference materials. Besides, positive Ce anomalies in all seawaters examined were also found, which could be attributed to the fact that Nozaki et al. regarded seawater filtered through a membrane filter with pore size of 0.04 μm as dissolved phase, while the submicron particles between 0.04 and 0.4 μm were thought to be acid-soluble matter or suspended particulate [3,17–19]. Accordingly, the oxidation of soluble Ce(III) to insoluble Ce(IV) resulted in relatively positive Ce anomaly in so-called suspended particulate as well as relatively negative Ce anomaly in so-called dissolved phase.

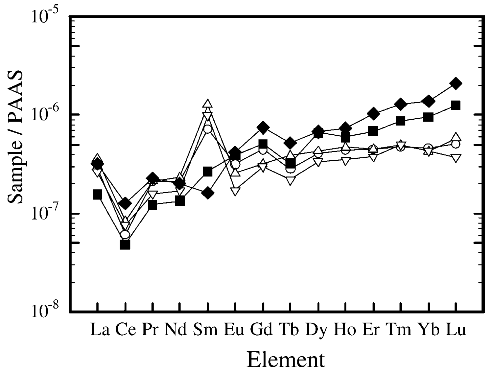

Fig. 1. PAAS-normalized REE distribution patterns for seawaters. (○) NASS-5; (△) CASS-3; (▽) CASS-4; (♦) Ise Bay coastal seawater; (■) Take Island coastal seawater.

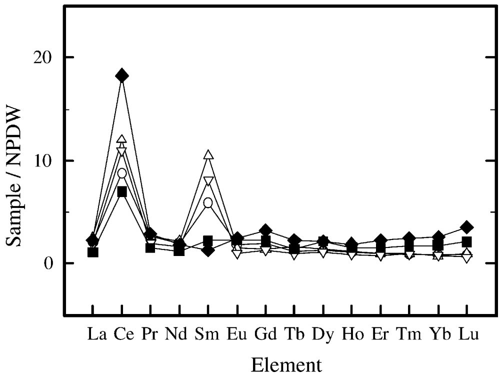

Fig. 2. NPDW-normalized REE distribution patterns for seawaters. (○) NASS-5; (△) CASS-3; (▽) CASS-4; (♦) Ise Bay coastal seawater; (■) Take Island coastal seawater.

Furthermore, it was considered that these Ce anomalies were amplified with increasing depth [19]. Consequently, when the REEs in so-called dissolved phase in deep seawater were used for normalization, seawaters filtered through a membrane filter with pore size of 0.45 μm, which were commonly regarded as dissolved phase, showed positive Ce anomalies.

4. Conclusion

The REEs in reference seawater materials, the Take Island coastal seawater, and the Ise Bay coastal seawater were determined by ICP-MS after preconcentration with a chelating resin-packed minicolumn. The results were evaluated with REE distribution patterns after shale-normalization and NPDW-normalization, respectively, in both of which slight enrichments of heavy REEs in the Take Island coastal seawater and the Ise Bay coastal seawater were observed in addition to Sm contaminations in all examined seawater reference materials. Positive Ce anomalies for all seawater samples examined were observed in NPDW-normalized REE distribution pattern, which depended on the dissolved states of REEs in seawater.

Acknowledgements

The present research has been supported partly by the Grant-in-Aid (No. 16002009) of the Specially Promoted Research and by COE Formation Basic Research of "Future-oriented Isotope Science" (2003–2004) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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