Bull. Chem. Soc. Jpn., **68**, 3065—3070(1995)

# Multielement Determination of Rare Earth Elements in Coastal Seawater by Inductively Coupled Plasma Mass Spectrometry after Preconcentration Using Chelating Resin

**Hideyuki Sawatari, Takeshi Toda, Tomoo Saizuka,# Chisen Kimata, Akihide Itoh, and Hiroki Haraguchi***

Department of Applied Chemistry, School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01

(Received April 13, 1995)

Rare earth elements in coastal seawater were preconcentrated by using chelating resin in a batch method and determined simultaneously by inductively coupled plasma mass spectrometry (ICP-MS). In this procedure, matrix components (Na, K, Mg, and Ca) were eliminated to reduce matrix effects in ICP-MS analysis and rare earth elements were concentrated by a concentration factor of 100. The pH dependence of the recovery, resin amounts, amount of ammonium acetate for washing, and elution of adsorbed metals with nitric acid were examined in details to optimize the experimental conditions in sample pretreatment. All rare earth elements in coastal seawater were determined at the ppt or sub-ppt level successfully by the present analytical method.

Rare earth elements (REEs) are a kind of key trace elements in earth sciences and their composition in magmatic rocks has been widely and routinely used in the study of geochemistry and evolution of the Earth.[1—4] REEs are also important for the study on geochemical processes in marine environment. The concentrations of REEs in seawater, in general, are extremely low, and hence the geochemical study of REEs in seawater has been restricted by analytical difficulties so far. The determination of REEs in seawater has been carried out mainly by neutron activation analysis (NAA)[5,6] or isotope dilution-thermal ionization mass spectrometry (ID-TIMS).[7—10]

Recently, inductively coupled plasma mass spectrometry (ICP-MS) is often used for the determination of REEs because of its high sensitivity, high selectivity, and high sample throughput.[11] The direct determination of REEs in seawater by ICP-MS, however, is still difficult because of high concentrations of salts and low concentrations of REEs. The concentrations of REEs in seawater are at the low ppt ($\mathrm{pg\,ml^{-1}}$) or sub-ppt level, which are close to or below the lower limit of determination obtained by ICP-MS. Besides the low concentrations of REEs, the salts in seawater at the high concentration level make it difficult to introduce seawater sample directly into the plasma, because matrix or memory effects cause serious problems in the ICP-MS measurements. As the result, preconcentration of REEs and elimination of salts are inevitably required for accurate and precise determination of REEs in seawater.

As preconcentration techniques for REEs in seawater, coprecipitation with iron hydroxide has been most often utilized prior to the measurement by NAA,[5] ID-TIMS,[7—10] or inductively coupled plasma atomic emission spectrometry (ICP-AES).[12] Also a chelating resin of Chelex® 100 was used for such purpose.[6] Chelex® 100 has been proved to be very effective and convenient for multielement preconcentration of trace elements in seawater by ICP-AES,[13—15] although precaution is required for elimination of magnesium and calcium from the resin because of their affinities with Chelex® 100 resin.[16] Recently the determination of REEs in seawater was performed by ICP-MS after solvent extraction with bis(2-ethylhexyl) hydrogen phosphate (HDEHP) and 2-ethylhexyl dihydrogen phosphate ($\mathrm{H_2MEHP}$),[17] coprecipitation with iron hydroxide,[18,19] and adsorption on $\mathrm{C_{18}}$-bonded silica gel.[20] However, it appears that these methods have some limitation and inconvenience in analysis. Möller et al.[21] reported the determination of REEs in seawater using Chelex® 100 and ICP-MS. Although they attained a preconcentration factor of 330 and successfully determined REEs in seawater, their method is rather time consuming because seawater sample was preconcentrated by a column method at very low flow rate. On the other hand, preconcentra-

---

#Present address: Nagoya Research Laboratory, Toray Research Center, Inc., Ohe-cho 9-1, Minato-ku, Nagoya 465.

tion using Chelex® 100 resin in a batch method could be performed for rather short time.[14] Hence, preconcentration using Chelex® 100 resin in a batch method for simultaneous multielement determination by ICP-MS has been investigated to establish the analytical method for REEs in seawater, using coastal seawater collected in the Nagoya port.

## Experimental

**Chemicals.** Chemicals used were of analytical reagent grade. Ammonium acetate aqueous solution was prepared with acetic acid and aqueous ammonia solution. The chelating resin of Chelex® 100 (100—200 mesh; Bio Rad Laboratories, Richmond, CA, USA) was kept in 5 M (M= mol dm$^{-3}$) hydrochloric acid (daily changed) for 5 d, and washed with water, 2 M nitric acid and water, in turn, before use. The resin thus precleaned was dried in a deccicator with silica gel. Purified water used throughout the present experiment was prepared by using a Milli-Q system (Nippon Millipore Ltd.).

**Instruments.** An ICP-MS instrument of model SPQ-8000 from Seiko Instrument Inc. (Tokyo) was used for the determination of REEs. Major elements (Na, K, Mg, Ca) in the seawater samples were determined by an inductively coupled plasma atomic emission spectrometer (Plasma AtomComp MKII from Jarrell-Ash, Franklin, MA, USA). The operating conditions of the ICP-MS and ICP-AES instruments are listed in Table 1 along with their components. The pH measurement of the sample solutions was performed by a pH meter (model CG822 from SCHOTT GERÄTE GmbH, Germany).

**Preconcentration Procedure.** Coastal seawater collected near the Nagoya port (Aichi Prefecture; 34°59′N, 136°49′E) was filtered with a membrane filter (0.45 μm) immediately after sampling, and acidified to pH 1—2 with nitric acid. Then the seawater sample was treated as follows: One liter of the acidified seawater sample was taken in a beaker, and then 0.8 g of chelating resin was added into it. Next, pH of the sample solution was adjusted to 6.0 with acetic acid or aqueous ammonia solution, followed by stirring with a magnetic stirrer for 2 h. The resin was collected on a glass filter (1.4 cm i.d.), and the resin on the filter was washed with small amount of water and 15 ml of 1 M ammonium acetate (pH 5.5) to eliminate Ca and Mg adsorbed on the resin. Furthermore, it was washed with 15 ml of water to clean up ammonium acetate, and then REEs were eluted with 9 ml of 2 M nitric acid. Finally the sample solution was diluted to 10 ml by adding 1 ml of the internal standard solution containing In and Re (100 ng ml$^{-1}$ each). Consequently, 100-fold preconcentration was achieved in the present preconcentration procedure. In the recovery test, 10 ml of the mixed standard solution containing all REEs (100 ng ml$^{-1}$ each) was added into 1 dm$^3$ of seawater sample solution, and the same pretreatment procedure as described above was carried out.

## Results and Discussion

In order to obtain accurate and precise analytical results, the efficient preconcentration of REEs should be performed before the ICP-MS measurement. In the present experiment, pH of sample seawater in adsorption procedure, the amount of chelating resin, elimination of Mg and Ca adsorbed on the resin, and elution efficiency for REEs from the resin may influence to achieve the better recoveries of REEs in preconcentration procedure and the analytical figures of merit for the present analytical method. Thus, such experimental conditions were optimized to obtain the better recoveries of REEs in seawater. In the following experiments, stirring time for adsorption of trace metals was 2 h, according to the results by Cheng et al.[14] who used 1 dm$^3$ of seawater sample and 0.3 g of Chelex® 100 resin.

Table 1. Instrumental Operating Conditions for ICP-MS and ICP-AES

| | |
|---|---|
| ICP-MS: Seiko SPQ-8000 | |
| Plasma conditions | |
| Incident power | 1.2 kW |
| Coolant gas flow rate | 16 L min$^{-1}$ |
| Auxiliary gas flow rate | 1.0 L min$^{-1}$ |
| Carrier gas flow rate | 0.50 L min$^{-1}$ |
| Sample uptake rate | 0.7 ml min$^{-1}$ |
| Nebulizer | Concentric type |
| Sampling conditions | |
| Sampling orifice diameter | 1.1 mm |
| Skimmer orifice diameter | 0.35 mm |
| Sampling position | 15 mm from load coil |
| Data acquisition | |
| Dwell time | 10 ms/ch |
| Data points | 3 points/peak[a)] |
| No. of scans | 100 |
| ICP-AES: Jarrell-Ash Plasma AtomComp MKII | |
| Plasma conditions | |
| Incident power | 1.0 kW |
| Coolant gas flow rate | 17 L min$^{-1}$ |
| Auxiliary gas flow rate | 1.0 L min$^{-1}$ |
| Carrier gas flow rate | 0.5 L min$^{-1}$ |
| Sample uptake rate | 1.2 ml min$^{-1}$ |
| Observation height | 18 mm above load coil |
| Nebulizer | Cross-flow type |
| Polychromator | |
| Mounting | Paschen-Runge |
| Focal length | 75 cm |
| Grating | 2400 grooves/mm |
| Entrance slit width | 25 μm |
| Exit slit width | 50 μm |

a) Assumed peak center and ±0.125 u from the center.

**pH Dependence of Recoveries of REEs.** The pH of sample seawater during the adsorbing procedure was optimized, because adsorption efficiencies of REEs on Chelex® 100 resin depended on pH of the sample solution. In Fig. 1, pH dependence of the recoveries of Y, La, Ce, Tb, and Lu are shown. The recoveries of all other REEs were similar to those shown in Fig. 1. The recoveries of REEs were higher than 80% in the pH range between 5—7, and became lower below pH 4. The highest recoveries were obtained at pH 6 for all REEs. Consequently, pH 6 was adopted for the pretreatment procedure as the optimum condition.

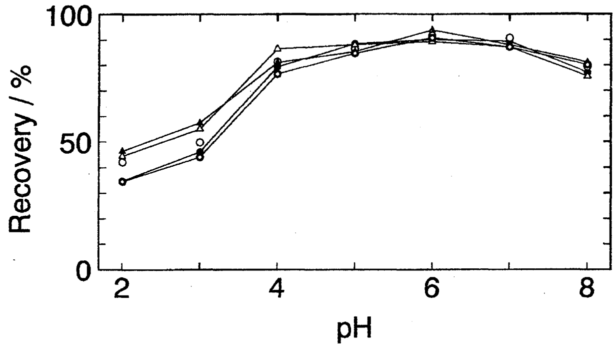

Fig. 1. pH Dependence of recoveries for Y (●), La (▲), Ce (○), Tb (△), and Lu (◎).

**Optimization of Resin Amount in Preconcentration.** In preconcentration, it is desirable to use minimum amount of chelating resin, because the following problems would be caused in analysis; i) large amounts of Mg and Ca are adsorbed on the resin which result in their high concentration remained in the analysis solution, ii) large amounts of ammonium acetate aqueous solution and nitric acid must be used for washing resin and elution of REEs, respectively, which may cause contamination from these reagents.

Dependence of the recoveries of Y, La, Ce, Tb, and Lu on the amount of the chelating resin are summarized in Table 2. As is seen in Table 2, the recoveries of REEs were almost constant above 0.8 g. Since all other REEs provided the similar results, 0.8 g of the resin was used for preconcentration of REEs in seawater.

**Elimination of Major Elements Adsorbed on Resin with Ammonium Acetate Solution.** When seawater is treated with Chelex® 100 resin, Mg and Ca are significantly adsorbed on the resin and they should be removed to minimize matrix effects in the ICP-MS measurement. It was reported that Mg and Ca retained on the resin could be removed by ammonium acetate aqueous solution,[12—16] although the use of excess amount of ammonium acetate solution causes loss of the analytes.

In the present experiment, the efficiency of removal of Mg and Ca was examined using ammonium acetate solution at various pH. The concentration of ammonium acetate was 1 M, whose pH was adjusted with aqueous ammonia solution or acetic acid. In this experiment, 15 ml of the ammonium acetate solution was used. The results are summarized in Table 3. Elimination of Mg and Ca was more effective with the ammonium acetate solution of lower pH, but loss of the analytes was more serious. Hence, pH of the ammonium acetate solution was adjusted at 5.5 as a compromised condition.

Table 2. Dependence of Recoveries for Y, La, Ce, Tb, and Lu on Chelating Resin Amount

| | Resin amount/g | | | | |
|---|---|---|---|---|---|
| Element[a)] | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 |
| Y | 76.3 | 86.8 | 90.2 | 88.6 | 88.7 |
| La | 79.5 | 87.3 | 91.6 | 91.8 | 93.0 |
| Ce | 81.2 | 88.5 | 93.9 | 91.5 | 93.0 |
| Tb | 78.2 | 85.2 | 89.4 | 87.8 | 88.9 |
| Lu | 80.7 | 87.1 | 90.8 | 89.2 | 89.8 |

a) The concentration of each REE in the test solution was 1 ppb.

Next, the effect of the amount of the 1 M ammonium acetate solution (pH 5.5) on effective removal of Mg and Ca was investigated. The results are summarized in Table 4. The use of 30 ml of the ammonium acetate solution was enough to remove Mg and Ca, but at the same time loss of the analytes occurred quite significantly. Thus, 15 ml of the 1 M ammonium acetate solution (pH 5.5) was used for elimination of Mg and Ca, although some matrix effect in ICP-MS measurement might be caused by Mg and Ca under this condition. In practical analysis, however, matrix effect due to Mg and Ca could be corrected by an internal standard method.

**Elution of REEs from Resin.** In order to elute REEs adsorbed on the resin, 2 M nitric acid was used as the eluent. All REEs were completely eluted from the resin with 9 ml of 2 M nitric acid, while only 60% of

Table 3. Concentrations ($\mu g\,ml^{-1}$) of Major Elements in Concentrated Seawater Samples (100-fold) after Washing with Ammonium Acetate Solution of Different pH

| Element | pH | | |
|---|---|---|---|
| | 5.0 | 5.5 | 6.0 |
| Na | 0.5 | 0.8 | 1.4 |
| K | N.D. | N.D. | N.D. |
| Mg | 37 | 49 | 115 |
| Ca | 163 | 211 | 318 |

Table 4. Dependences of Major Element Concentrations in Concentrated Seawater (100-fold) and Recoveries of REEs on Volume of Ammonium Acetate Solution Used for Washing

| | Volume of ammonium acetate soln./ml | | | |
|---|---|---|---|---|
| Element | 0 | 15 | 30 | 45 |
| Concentration of major element/$\mu g\,ml^{-1}$ | | | | |
| Na | 236 | 0.7 | 0.4 | 0.4 |
| K | 8.4 | N.D. | N.D. | N.D. |
| Mg | 1140 | 61 | 10 | 7 |
| Ca | 796 | 217 | 47 | 12 |
| Recovery of REE/% | | | | |
| Y | 92.8 | 90.2 | 83.1 | 81.2 |
| La | 100.1 | 91.6 | 86.2 | 85.1 |
| Ce | 102.2 | 93.9 | 88.2 | 88.5 |
| Tb | 97.3 | 89.4 | 82.5 | 84.0 |
| Lu | 95.6 | 90.8 | 86.2 | 87.2 |

a) The concentration of each REE in the test solution was 1 ppb.

them was eluted with 5 ml of the eluent. Hence, it was decided to use 9 ml of 2 M nitric acid for the elution of REEs. Since elution was complete with 9 ml of the eluent, REEs in 1 $dm^3$ of the sample could be concentrated by 100-times without evaporation procedure to reduce the volume of the analysis solution.

**Correction of Matrix Interferences due to Major Elements.** The matrix effects (suppression in sensitivity) and instrumental drift were corrected by an internal standard method. The concentrations of major elements in the analysis solution which was finally obtained in the preconcentration procedure, are shown in Table 4. As the internal standard elements, In and Re were used because the masses of In and Re are slightly smaller and larger than those of REEs, respectively. The correction by the internal standard method was carried out in a similar manner to the previous reports.[22,23] When 200 ppm of Ca coexisted in the analysis solution, the sensitivities of the analytes were reduced by about 20% compared to those in the matrix-free solution. Since the magnitude of the sensitivity suppression was almost the same for all REEs, In, and Re, correction by the internal standard method could be carried out as usual.[22,23]

In the determination of REEs by ICP-MS, interferences with heavy-REEs from oxide ions of light-REEs have been pointed out as a problem, and several methods to reduce or correct such interferences have been proposed.[21,24—26] In the present study, however, interference correction for the oxide ions of light-REEs was not carried out, because the differences in the concentrations of light-REEs and heavy-REEs in usual seawater are within one order of magnitude and hence the oxide interference was negligibly small.

Also Ba in the analysis solution is a potential source of spectral interferences, because $^{151}Eu^+$ is interfered by $^{135}Ba^{16}O^+$ and the concentration of Ba in seawater is much higher than those of REEs. In the present study, Ba was eliminated by the pretreatment and the concentration of Ba in the analysis solution was lower than 10 ppb. The analytical error of Eu caused by Ba at this concentration level was estimated to be less than 3% for the seawater sample analyzed in the present study, and hence correction for $BaO^+$ was not carried out.

**Analytical Figures of Merit.** The recoveries of REEs obtained by the present method are summarized in Table 5. The values in Table 5 are the mean values and the standard deviation estimated from the repeated experiment (4 times). The recovery values were about 90%, and their reproducibilities were less than 2.3%.

Shimizu et al.[27] discussed on the recovery of REEs from seawater in their study on isotopic ratio of Ce and Nd and REE patterns in seawater. They concluded that the recoveries of heavy-REEs obtained by $MnO_2$-coated fiber were lower than those for light-REEs. In the present method using chelating resin, the recoveries of light-REEs and heavy-REEs were not significantly different from each other, as is seen in Table 5.

Table 5. Recovery of Rare Earth Elements Evaluated by Using Spiked Seawater Sample

| Element[a] | Recovery[b] % |
|---|---|
| Y | 90.2 ± 0.9 |
| La | 91.6 ± 0.9 |
| Ce | 93.9 ± 0.3 |
| Pr | 91.7 ± 1.0 |
| Nd | 90.4 ± 0.1 |
| Sm | 89.5 ± 1.1 |
| Eu | 87.8 ± 0.3 |
| Gd | 89.3 ± 2.3 |
| Tb | 89.4 ± 1.0 |
| Dy | 89.6 ± 1.4 |
| Ho | 89.0 ± 0.8 |
| Er | 90.8 ± 0.9 |
| Tm | 90.6 ± 0.7 |
| Yb | 90.3 ± 1.0 |
| Lu | 90.8 ± 0.9 |

a) The concentration of each REE in the test solution was 1 ppb. b) The mean and standard deviation estimated from 4-times repeated preconcentration.

In Table 6, the instrumental and analytical detection limits obtained by the present method are summarized, along with the masses of the isotopes used for the ICP-MS measurement. The instrumental detection limits were obtained for pure standard solutions without preconcentration. They were defined as the concentration corresponding to 3 times of the standard deviation of the blank signal intensity, which was estimated from the 10-times duplicate measurements of the blank solution. The analytical detection limits in Table 6 were calculated from the instrumental detection limits, taking into account the concentration factor (100) and the recoveries shown in Table 5.

The blank values in the present method are also summarized in Table 6. To estimate the blank values, 1 $dm^3$ of 0.1 M nitric acid was used as the test solution, and the preconcentration and measurement procedures similar to the present method were carried out. Except for Y and La, the blank values were at the same level as or lower than the analytical detection limits. Even for Y and La, the blank values were almost negligible because they were much lower than the abundances of these elements in the sample seawater.

**Concentration of REEs in Coastal Seawater.** The analytical results for coastal seawater collected near Nagoya port are presented in Table 7. These results were obtained by the ICP-MS measurement after the preconcentration procedure described in the experimental section, where correction in terms of the recoveries were made. The concentrations in Table 7 are the means of the repeated preconcentration procedures and measurements (4 times). By the present method, REEs in seawater at the sub-ppt level could be determined

Table 6. Detection Limits and Blank Values for Rare Earth Elements

| Element | Isotope measured<br>u | Instrumental detection limit[a]<br>pg ml$^{-1}$ | Analytical detection limit[b]<br>pg ml$^{-1}$ | Blank<br>pg ml$^{-1}$ |
|---|---|---|---|---|
| Y | 89 | 0.74 | 0.0083 | 0.12 |
| La | 139 | 0.46 | 0.0051 | 0.051 |
| Ce | 140 | 1.6 | 0.017 | 0.094 |
| Pr | 141 | 0.24 | 0.0027 | 0.0082 |
| Nd | 146 | 1.71 | 0.019 | N.D. |
| Sm | 147 | 3.0 | 0.034 | 0.046 |
| Eu | 151 | 1.1 | 0.012 | 0.013 |
| Gd | 157 | 1.2 | 0.013 | N.D. |
| Tb | 159 | 0.15 | 0.0016 | 0.0022 |
| Dy | 163 | 0.98 | 0.011 | 0.021 |
| Ho | 165 | 0.10 | 0.0012 | 0.0027 |
| Er | 168 | 0.54 | 0.0060 | 0.017 |
| Tm | 169 | 0.28 | 0.0031 | 0.0076 |
| Yb | 174 | 1.1 | 0.012 | 0.016 |
| Lu | 175 | 0.15 | 0.0016 | N.D. |

a) Detection limit obtained for standard solutions without preconcentration.
b) Detection limit obtained after preconcentration by the present chelating resin method.

Table 7. Analytical Results for REEs in Coastal Seawater

| Element | Concentration[a]<br>pg ml$^{-1}$ |
|---|---|
| Y | 42.4 ± 1.0 |
| La | 11.5 ± 0.3 |
| Ce | 9.51 ± 0.28 |
| Pr | 1.89 ± 0.06 |
| Nd | 8.61 ± 0.24 |
| Sm | 1.69 ± 0.06 |
| Eu | 0.30 ± 0.01 |
| Gd | 2.31 ± 0.09 |
| Tb | 0.38 ± 0.01 |
| Dy | 2.85 ± 0.10 |
| Ho | 0.80 ± 0.02 |
| Er | 2.80 ± 0.07 |
| Tm | 0.47 ± 0.01 |
| Yb | 3.42 ± 0.12 |
| Lu | 0.60 ± 0.01 |

a) Mean and relative standard deviation obtained from 4 times repeated preconcentration procedure.

with precision of 2—4%.

In Fig. 2, the abundances of REEs in the coastal seawater determined in the present study are shown as a shale-normalized REE abundance pattern, together with the data in the previous studies.[6,9,10] The REE abundances of shale, which are considered to represent the REE abundances of the continental crust, are often used for the normalization in marine geochemistry, while chondrite-normalized REE pattern (Masuda–Coryell plotting)[2,3] is mostly used in geological and geochemical studies. Here, the REE abundances of the Post-Archean Average Australian Shale[4] were employed for normalization, as suggested by McLennan.[28]

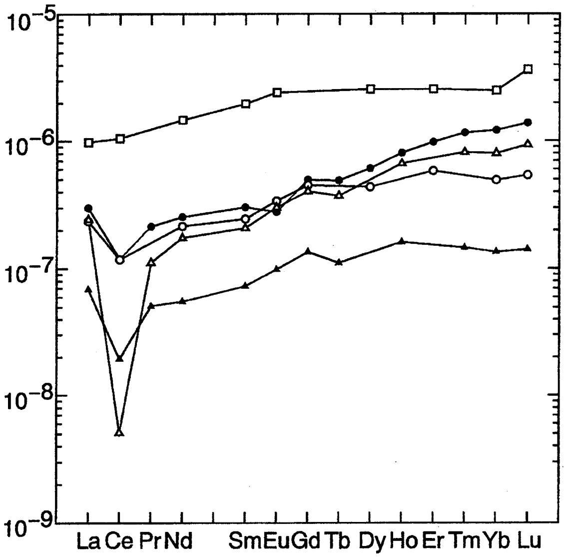

Fig. 2. Shale(PAAS)-normalized REE patterns for seawater and river water. ●, Nagoya Port (present work); ○, surface seawater near Kyushu Island, Japan (Ref. 10); ▲, Pacific Ocean, 15 m depth (Ref. 6); △, Pacific Ocean, 3250 m depth (Ref. 6); □, Shinano River, Japan (Ref. 9).

It is seen from Fig. 2 that the concentrations obtained in the present study are at almost the same level as those in the previous reports, and the shale-normalized REE pattern shows heavy-REEs enriched features, which is often observed for seawater. The concentrations of heavy-REEs, however, are higher and the inclination of heavy-REEs span is steeper than other REE patterns for seawaters. As for light-REEs, the concentrations for the present sample and those collected in near-shore area of Kyushu Island[10] are at almost the same level, but the concentrations and the inclination of the pattern for heavy-REEs are slightly different, as is seen in Fig. 2. Considering the sampling site, it is plausible that the present seawater sample was influenced by the inflow of fresh river water. It is seen that the concentration of Na in the present coastal seawater was 8060 ppm, while it is 10800 ppm in typical seawater.[29)] The REE patterns of the present study, however, is quite different from those of river water reported in the previous study.[9)] As an example, the REE pattern of the Shinano river water[9)] is shown in Fig. 2. In order to investigate and understand the REE pattern of the present study, more comprehensive studies on the determination of REEs in the seawater and the river water should be required in future.

## Conclusion

Rare earth elements at the ppt or sub-ppt level in coastal seawater were successfully determined by ICP-MS using chelating resin preconcentration. The present Chelex® 100 resin preconcentration method provided the recoveries for all REEs about 90% and good reproducibility. In addition, employing the present batch method, the time required for the pretreatment is significantly saved compared to those for the preconcentration by the column method using the chelating resin. The shale-normalized REE distribution pattern of the present data for coastal seawater showed marked difference from those for open seawater as well as for river water. Further comprehensive studies on the REE distribution patters in aqua environment including sediment samples are required to elucidate the distributions of REEs and their geochemical cycles in the biosphere.

### References

1) A. Masuda, *J. Earth Sci., Nagoya Univ.*, **10**, 173 (1962).

2) C. D. Coryell, J. W. Chase, and J. W. Winchester, *J. Geophys. Res.*, **68**, 559 (1963).

3) A. Masuda and Y. Matsui, *Geochim. Cosmochim. Acta*, **30**, 239 (1966).

4) "Geochemistry and Mineralogy of Rare Earth Elements," in "Reviews in Mineralogy," ed by B. R. Lipin and G. A. McKay, Vol. 21, The Mineralogical Society of America, Washington, D. C. (1989).

5) E. D. Goldberg, M. Koide, R. A. Schmitt, and R. H. Smith, *J. Geophys. Res.*, **68**, 4209 (1963).

6) H. J. W. DeBaar, M. P. Bacon, P. G. Brewer, and K. W. Bruland, *Geochim. Cosmochim. Acta*, **49**, 1943 (1985).

7) A. Masuda and Y. Ikeuchi, *Geochem. J.*, **13**, 19 (1979).

8) H. Elderfield and M. J. Greaves, *Nature*, **296**, 214 (1982).

9) S. J. Goldstein and S. B. Jacobsen, *Earth Planet. Sci. Lett.*, **89**, 35 (1988).

10) M. Tanaka, H. Shimizu, and A. Masuda, *Geochem. J.*, **24**, 39 (1990).

11) "An Application of Inductively Coupled Plasma Mass Spectrometry," ed by A. R. Date and A. L. Gray, Blackie (1989).

12) H. Daidoji, S. Tamura, and M. Matsubara, *Bunseki Kagaku*, **34**, 340 (1985).

13) C. J. Cheng, T. Akagi, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **58**, 3229 (1985).

14) C. J. Cheng, T. Akagi, and H. Haraguchi, *Anal. Chim. Acta*, **198**, 173 (1987).

15) T. Akagi and H. Haraguchi, *Bunseki Kagaku*, **36**, 688 (1987).

16) H. M. Kingston, I. L. Barnes, T. J. Brady, T. C. Rains, and M. A. Champ, *Anal. Chem.*, **50**, 2064 (1978).

17) M. B. Shabani, T. Akagi, H. Shimizu, and A. Masuda, *Anal. Chem.*, **62**, 2709 (1990).

18) S. Westerlund and P. Öhman, *Deep-Sea Res.*, **39**, 1613 (1992).

19) G. Klinkhammer, C. R. German, H. Elderfield, M. J. Greaves, and A. Mitra, *Mar. Chem.*, **45**, 179 (1994).

20) M. B. Shabani, T. Akagi, and A. Masuda, *Anal. Chem.*, **64**, 737 (1992).

21) P. Möller, P. Dulski, and J. Luck, *Spectrochim. Acta, Part B*, **47B**, 1379 (1992).

22) W. Doherty, *Spectrochim. Acta, Part B*, **44B**, 263 (1989).

23) H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal. Sci.*, **11**, 369 (1995).

24) F. E. Lichte, A. L. Meier, and J. G. Crock, *Anal. Chem.*, **59**, 1150 (1987).

25) N. Shibata, N. Fudagawa, and M. Kubota, *Anal. Chem.*, **63**, 636 (1991).

26) P. Dulski, *Fresenius' J. Anal. Chem.*, **350**, 194 (1994).

27) H. Shimizu, K. Tachikawa, A. Masuda, and Y. Nozaki, *Geochim. Cosmochim. Acta*, **58**, 323 (1994).

28) S. M. McLennan, *Geochim. Cosmochim. Acta*, **58**, 2025 (1994).

29) Y. Nozaki, *Chikyukagaku* (*Geochemistry*), **26**, 25 (1992).