ANALYTICAL SCIENCES 2001, VOL.17 SUPPLEMENT

2001 © The Japan Society for Analytical Chemistry

Determination of Rare Earth Elements in Seaweed and Seawater Samples on the coast in Niigata Prefecture by ICP-MS after Solvent Extraction

Naoki KANO,[1†] Yoshitaka AOYAGI,[2] and Hiroshi IMAIZUMI[1]

[1†] *Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2-nocho, Niigata 950-2181, Japan (E-mail: kano@eng.niigata-u.ac.jp)*

[2] *Graduate School of Science and Technology, Niigata University, Ikarashi 2-nocho, Niigata 950-2181, Japan*

In order to investigate the present state of marine environment in Niigata Prefecture, to investigate the biological concentration in the ocean, and to investigate the behavior of rare earth elements (REEs) in the ocean, REEs in many kinds of seaweed samples as well as seawater samples in Niigata Prefecture were determined by ICP-MS. From the above-mentioned, the following matters have been clarified. (1) The concentrations of REEs are largely varied depending on the species of seaweed even in the same phylum (e.g., green algae, brown algae, or red algae). (2) The concentrations of REEs in the seaweed is about 10^3～10^5 times of that in the sea water; and.the enrichment factors of REEs is generally larger in HREE than LREE. (3) Positive Ce-anomaly was found in REE patterns of most seaweed samples, whereas negative Ce-anomaly was found in seawater sample. (4) Yb-anomaly as well as Ce-, and Eu-anomaly was also found in REE pattern of some seaweed and seawater samples taken on the coast in Niigata Prefecture. (5) REE pattern of seaweed samples may be an useful tracer of investigating the surrounding marine environments.

(Received on August 7, 2001; Accepted on September 13, 2001)

Until now, the determination of trace metals in marine organism are noted for investigating the marine environment.[1] Moreover, marine organisms such as the seaweed become the research object noticed as biological concentration.[2] Recently, it is reported that rare earth elements (REEs) may become important tracers for studying the circulation of materials in biosphere[3, 4] with the development of the analytical technique.

In the seaweed, there is the phylum such as green algae, brown algae, and red algae, and each phylum has over several decade types respectively.[5] It is considered that the difference of colors in the seaweed is due to the difference for the composition of photosynthetic pigment, so it may reflect the difference for the constituent of each seaweed. That is to say, systematic chemical analysis of various kinds of seaweed samples is particularly interesting.

From the above-mentioned, the determination of REEs in the seaweed sample seems to have the large significance from the viewpoint of environmental chemistry. As a chemical analysis of the seaweed from the determination of REEs pattern, there are examples of Onaga Bay in Miyagi Prefecture by Iwata et al. [6] and of Aburatsubo Bay in Miura Peninsula by Fu et al. [7] until now.

The coast in the vicinity in Niigata Prefecture locates in the geographic position which receives the effect of both the cold current and warm current systems in the ocean, so various kinds of biological samples exist. However, in Niigata Prefecture, only few works concerning the determination of REEs in environmental samples have been performed. Therefore, it seems to have considerably been left in the room of the research.

Considering the above-mentioned, REEs concentrations in some seaweed samples taken on the coast in Niigata Prefecture were determined in previous work.[8] In this work, REEs concentrations in the surrounding seawater (in addition to the seaweed samples) were also preliminary determined to investigate the biological concentration.

The main objective of this study is: (1) to investigate what kind of the REE pattern is obtained for marine environmental samples in Niigata prefecture depending on the type of seaweed and collected place; (2) to clarify the behavior of the rare earth element at marine environment in Niigata prefecture; (3) to survey the environmental state in Niigata Prefecture from REE pattern of marine environmental samples.

Experimental

Samples

Seaweed samples taken in August 2000 were listed in previous reports.[8] Additional samples taken in May 2001 are shown in Table 1. Moreover, the sampling of the seawater have been also carried out in this year to investigate the biological concentration comparing the concentrations of REEs in seaweed with that in seawater. The sampling locations for these samples are presented in Fig.1. In this year, the sampling has been performed at the coast in Hunae Town ((2) in Fig.1) and the coast in Kasiwazaki City ((5) in Fig.1) at the present time.

Instrumentation

An ICP-MS instrument (HP4500; Yokogawa Analytical systems, Tokyo) was used for determining rare earth elements (REEs) in seaweed and seawater samples. The operating condition of ICP-MS are shown in Table 2. The measured isotope of each REE is the same as that mentioned above.[8]

Table 1 Description of seaweed samples

Sample No.	Species	Sampling location
Chlorophyta	(Ryokuso)	
CN '01-1	*Ulva conglobata*	Hunae
CN '01-2	*Ulva conglobata*	Kashiwazaki
CN '01-3	*Chaetomorpha moniligera*	Hunae
Phaeophyta	(Kasso)	
PN '01-1	*Sargassum tortile*	Hunae
PN '01-2	*Sargassum tortile*	Kashiwazaki
Rhodophyta	(Koso)	
RN '01-1	*Grateloupia filicina*	Hunae
RN '01-2	*Grateloupia elliptica*	Hunae
RN '01-3	*Grateloupia elliptica*	Kashiwazaki
RN '01-4	*Grateloupia okamurai*	Hunae
RN '01-5	*Nemalion multifiduma*	Hunae

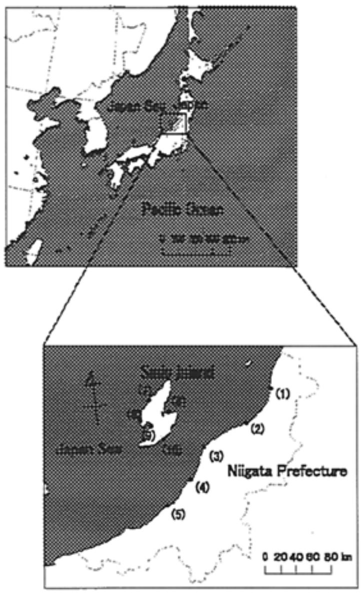

Fig. 1 Location of sampling points.

Table 2 Operating conditions of ICP-MS

Experimental parameter	Value
RF power	1400 W
Plasma gas flow	15 *l* /min
Carrier gas flow	1.2 *l* /min
Sampling depth	6.5 mm
Sample uptake rate	0.5 m*l* /min
Measurement point	3 points /peak
Integration time	1.0 sec /point

Chemicals

REEs standard solutions (XSTC-1) used for making the calibration curve were purchased from SPEX CertiPrep, Inc. (USA). Other reagents used in this work are the same as mentioned in previous reports.[8]

Preconcentration procedure of REEs

Each seaweed sample was decomposed with HNO_3 and $HF/HClO_4$ after Sakao et al.[9] The decomposition method is also the same as mentioned above.[8] Each seawater sample was filtered with a membrane filter immediately after sampling. REEs in the decomposed seaweed sample solution (or seawater) was preconcentrated with solvent extraction method.[10,11] The separation procedure for REEs, which is based on Shabani et al.[10], is shown in Fig. 2. After separating, the concentrations of REEs were determined by ICP-MS.

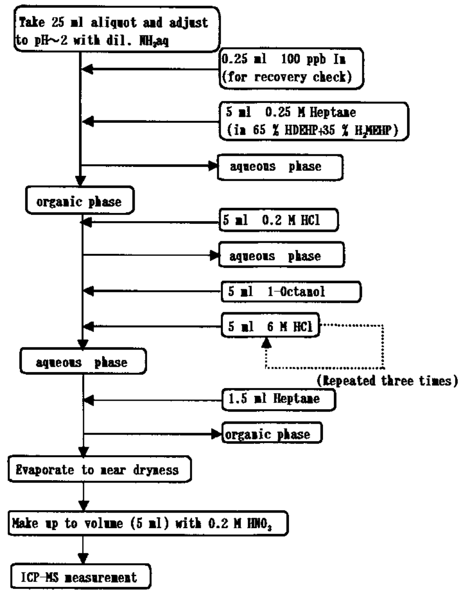

Fig. 2 Schematic of separation procedure for REEs.

Results and Discussions

REE concentrations in seaweed samples in Niigata prefecture

The concentrations of REEs in seaweed samples taken in this year on two coasts in Niigata prefecture are shown in Table 3 (Table 3a: green algae, Table 3b: brown algae, Table 3c: red algae). The relative standard deviation (RSD) of the three replicated analyses of each sample was less than 10%.

It indicates that the concentrations of REEs are largely varied depending on the species of seaweed even in the same phylum (e.g., green algae, brown algae, or red algae).

REE patterns in seaweed samples in Niigata prefecture

Normalized REE concentrations (REE patterns) in seaweed samples were shown in Fig. 3 (Fig. 3a: green algae, Fig. 3b: brown algae, Fig. 3c: red algae). The set of normalizing values (the concentrations of REEs in chondrite) used in this study was assigned from the values reported by Masuda.[12]

From Fig. 3, the following features have been found in REE patterns of seaweed samples taken on two coasts in this year : 1) Normalized REE concentrations of seaweed samples were generally enriched in the LREE relative to the HREE. 2) Positive Ce-anomaly, negative Eu-anomaly and negative Yb-anomaly were found for most seaweed samples. 3) Definitive difference between each phylum (e.g., green algae, brown algae, or red algae) was not observed.

In our previous studies[8], five types of different REE patterns were observed in seaweed samples taken in Niigata prefecture last year, and a large difference was found between REE pattern of the seaweed samples taken on some coasts in Niigata Mainland and that taken on some coasts in Sado Island.

The above-mentioned REE patterns observed in the samples taken this year are similar to that in the samples taken last year in Niigata Mainland. It can be considered that these patterns show peculiar features of the sample on the coasts in Niigata Mainland.

Table 3a The concentrations (ng・g^{-1}) of REEs in green algae

Sample No. REEs	CN '01- 1	CN '01-2	CN '01- 3
La	173	302	210
Ce	456	761	510
Pr	24.8	63.8	39.8
Nd	83.0	2.40	165
Sm	13.4	48.7	27.9
Eu	4.80	12.8	7.03
Gd	18.1	63.1	41.2
Tb	2.97	9.17	5.74
Dy	9.67	49.2	23.5
Ho	2.43	10.5	5.78
Er	9.12	30.0	15.5
Tm	1.00	4.62	2.29
Yb	7.60	23.6	8.18
Lu	1.21	4.59	2.24

Table 3b The concentrations (ng・g^{-1}) of REEs in brown algae

Sample No. REEs	PN '01- 1	PN '01 -2
La	196	181
Ce	611	557
Pr	44.2	30.8
Nd	181	112
Sm	47.8	19.5
Eu	10.8	8.31
Gd	44.9	32.1
Tb	8.19	4.17
Dy	39.4	17.9
Ho	8.43	5.11
Er	24.1	13.6
Tm	4.58	1.45
Yb	22.1	7.66
Lu	4.02	2.99

Table 3c The concentrations (ng・g^{-1}) of REEs in red algae

Sample No. REEs	RN '01 –1	RN '01 –2	RN '01 –3	RN '01 –4	RN '01 –5
La	326	159	102	76.1	748
Ce	943	726	456	385	1.58E+3
Pr	49.1	25.7	27.8	14.4	131
Nd	191	93.0	112	59.5	455
Sm	34.3	15.1	27.7	11.4	76.2
Eu	8.58	4.38	7.45	3.73	10.4
Gd	44.9	16.8	26.8	17.1	55.7
Tb	6.57	2.28	4.16	2.55	8.68
Dy	30.2	12.8	21.3	15.2	37.3
Ho	6.81	3.31	3.35	3.82	8.44
Er	15.7	7.53	13.3	6.13	21.6
Tm	2.29	2.03	2.09	1.89	3.34
Yb	8.35	5.32	12.7	4.46	15.3
Lu	1.95	1.32	1.85	1.23	3.12

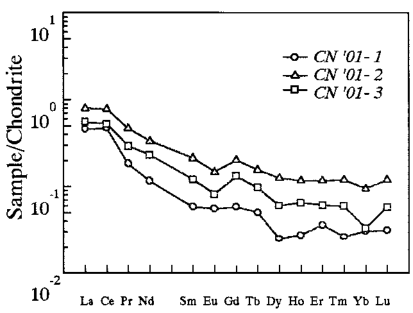

Fig. 3a Normalized REE concentrations for green algae.

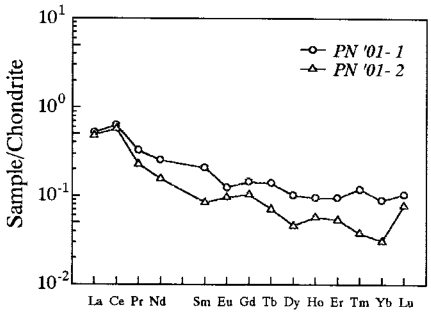

Fig. 3b Normalized REE concentrations for brown algae.

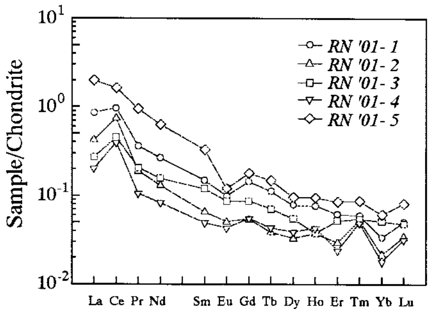

Fig. 3c Normalized REE concentrations for red algae.

Yb-anomaly

It is well-known that Eu-anomaly was found for REE patterns of some geochemical and/or environmental samples such as groundwater[13], rock, etc. when REE concentrations were normalized to CI chondrite (The data of CI chondrite is referred to Masuda[12]). Moreover, Ce-anomaly was found for some environmental samples such as seawater.[14, 15] However, for REE patterns of these samples mentioned above, Yb-anomaly has been little reported.

In our previous reports[8], it was suggested that Yb-anomaly was also found as well as both Ce- and Eu-anomaly in REE pattern of some seaweed samples taken on the coast in Niigata Prefecture. In addiition, as for REE patterns of seawater samples as well as some seaweed taken this year, Yb-anomaly was found.

It is considered that Yb (as well as Eu) is apt to be reduced to the divalent state from the trivalent state under the reducing conditions. Therefore, it is supposed that Yb-anomaly has appeared as "negative-anomaly" in REE pattern of some samples taken on the coast in Niigata Prefecture.

Comparing REE patterns of seaweed samples with that of seawater samples on the coast in Niigata prefecture

Normalized REE concentrations (REE patterns) in seawater sample on the coast in Kashiwazaki was shown in Fig. 4 along with that in some seaweed samples taken in the same place.

From this figure, it was found that 1) the concentrations of REEs in the seaweed is about $10^3 \sim 10^5$ times of that in the sea water; 2) the enrichment factors of REEs is generally larger in HREE than LREE.

That is to say, biological concentration was clearly found in marine environmental samples in Niigata prefecture.

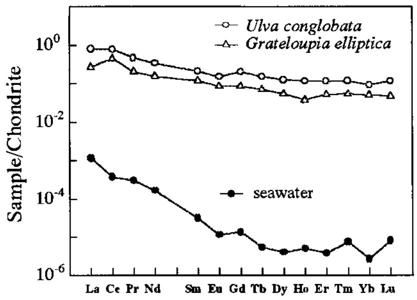

Fig. 4 Normalized REE concentrations for seaweed and seawater samples on the coast in Kashiwazaki.

Moreover, slightly negative Ce-anomaly was found in REE pattern of seawater sample in contrast to positive Ce-anomaly observed in REE patterns of most seaweed samples.

It is known that Ce in seawater tends to oxidize from the trivalent state (as unstable dissolved material) to the tetravalent state (as solid $Ce(OH)_4$). The property of Ce would explain the phenomenon observed as "Ce-anomaly" in REE pattern of seawater and seaweed samples.

From above-mentioned, it has been considered that REE pattern of seaweed samples as well as seawater may be useful to investigate the surrounding marine environments.

Acknowledgements

The authors are grateful to Dr. K. Satoh of Fac.of Sci. in Niigata University for permitting the use of the facilities and instruments, and for giving helpful advice in measurement. The authors would also like to thank Prof. K. Ohwada and Mr. M. Tsutumi of Ocean Research Institute, the University of Tokyo, and to thank Dr. J. Zhang of Fac. of Sci. in Toyama University for giving helpful advice in experiment.

References

1. T. Yamamoto, *Kaiyokagakukenkyu*, **1995**, *8(1),* 21.
2. S. Gohda and H.Yamazaki, *Kaiyo Monthly*, **1989**, *21(3)*, 136.
3. T. Akagi and F.F. Fu, *Bunseki*, **2000**, *8*, 453.
4. J. Zhang, T. Ishii, and K. Fujikura, *Chinese Science Bulletin*, **1999**, *44*, 258.
5. S. Arazaki, in "*KaisoBentosu*", ed. M. Iwashita, **1992**, Tokai Univ., Tokyo, 36.
6. Y. Iwata, H. Imura and N. Suzuki, *J. Radioanal. Nucl. Chem.*, **1993**, *172(2)*, 305.
7. F.F. Fu, T. Akagi, S. Yabuki, M. Iwaki, and N. Ogura, *J. Phycol.*, **2000**, *36*, 62.
8. N. Kano, Y. Aoyagi, and H. Imaizumi, *Kankyo Kagaku (J. Environ. Chem.)*, **2001**, *11*, 221.
9. S. Sakao, Y. Ogawa, and H. Uchida, *Anal. Chim. Acta*, **1997**, *355*, 121.
10. M. B. Shabani, T. Akagi, H. Shimizu, and A. Masuda, *Anal.Chem.*, **1990**, *62*, 2709.
11. V. K. Panday, K. Hoppstock, J. S. Becker, and H. J. Dietze, *Atomic Spectroscopy*, **1996**, *17*, 98.
12. A. Masuda, in "*GansekiKobutsu no Chikyukagaku*", ed. Y. Matsui and S. Sakano, **1979**, Iwanami Shoten, Tokyo, 244.
13. A. Masuda, O. Kawakami, Y. Dohmoto, and T. Takenaka, *Geochem. J.*, **1987**, *21*, 119.
14. J. Zhang, *Kaiyo Monthly*, **1998**, *30(1)*, 12.
15. H. J. W. De Baar, M. P. Bacon, P. G. Brewer, *Nature*, **1983**, *301*, 324.