

Determination of Rare Earth Elements, Thorium and Uranium in Seaweed Samples on the Coast in Niigata Prefecture by Inductively Coupled Plasma Mass Spectrometry

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Abstract

The determination of rare earth elements (REEs), thorium (Th), and uranium (U) in seaweeds of various species and in ambient surface seawater were performed by inductively coupled plasma mass spectrometry (ICP-MS). The seaweeds and the seawater samples were collected at 10 different coastal areas of Niigata Prefecture in Japan twice a year (spring and autumn) in 2004 and 2005.

Results showed that, concentration of REEs in seaweed species from Niigata Prefecture were about 10^2 - 10^3 times higher than those in seawater ; and the enrichment factors of REEs was larger in heavy REE than light REE. A significant concentrations difference of REEs, Th, U was found among species even in the same phylum. The concentration of U in *Undaria pinnatifida* was the highest. Considering the experimental result that *Undaria pinnatifida* has low concentration of REEs among typical brown algae, different REEs and U uptake mechanisms were suggested. The concentration of REEs, Th and U did not vary remarkably among sampling points and/or seasons.

[Keywords]: Seaweed sample, Seawater sample, Rare earth elements (REEs), Niigata Prefecture, ICP-MS

1. Introduction

Seaweeds are traditionally used in the orient as part of the daily diet and as excellent source of iodine (Netten et al., 2000). Consumption of particular seaweeds of various species of edible green, brown and red algae is high in Asia, especially in Japan, China and Korea. Seaweeds are sources of protein and carbohydrates, although these nutrients content in some seaweed varies with species and environment. Seaweeds have also been used in the pharmaceutical, cosmetics and food industries (Marinho-Soriano et al., 2006). Moreover, biosorption studies using living biomass including seaweed have been widely performed in large parts of the world (e.g., Seki and Suzuki, 1998; Diniz and Volesky, 2005; Mohanty et al., 2006).

Determination of rare earth elements (REEs) in marine organisms such as seaweeds is important in studying the extent of these REEs to marine environment. REEs are considered important tracers for studying the circulation of materials in the biosphere (e.g., Zhang et al., 1999; Akagi and Fu, 2000). Our knowledge about REEs has increased due to developments of new analytical techniques.

Thorium (Th) and uranium (U), on the other hand, are natural radionuclides and sources of nuclear power (e.g., Harmsen et al., 1980). These elements are widely distributed in nature, and are possible harmful pollutants in the environment. Hence,

investigating the concentrations of Th and U in the environment is necessary from a radiation and pollution protection viewpoints (e.g., Matsuba et al., 2000).

The coasts in the vicinity of Niigata Prefecture (Hokuriku District, Japan) are located in the geographic position where both the cold ocean and the warm ocean current systems affect; so various kinds of marine organisms exist. However, as for the studies of seaweed in Japan, most of previous works were conducted on the Pacific Coast, and the chemical data of seaweed on the Coast of Japan Sea are extremely limited. To our knowledge, only few works were done on the determination of REEs, Th and U in seaweeds and seawater about the coasts of Niigata Prefecture.

Considering the above-mentioned, we mainly determined the concentrations of REEs in some seaweeds taken on the coast of Niigata Prefecture in previous paper (Kano et al., 2001), and consequently deduce some general characteristics concerning the behavior of REEs in seaweed in Niigata Prefecture coasts.

In addition to REEs, the concentration of Th and U in various species of seaweed and seawater samples in Niigata Prefecture were also determined by inductively coupled plasma mass spectrometry (ICP-MS) in this paper. Moreover, the uptake mechanisms of these elements into the seaweeds are also discussed from the comparison with the analytical results of REEs, Th and U among species (or phylum).

2. Experimental

2.1 Samples

Eighty three (83) healthy looking seaweeds samples [29 seaweeds species 4 green algae (10 samples), 16 brown algae (52 samples), 9 red algae (21 samples)] were sampled along several coasts in Niigata Prefecture (Fig.1) once in every spring and autumn in 2004 and 2005. All samples were sampled at rock reef about 100m from the coast. For example, *Sargassum hemiphyllum* and *Ulva pertus* grew on rocks by littoral zone. On the other hand, *Undaria pinnatifida* grew on rocks under the littoral zone to infralittoral zone. They are general species in the coast of Niigata prefecture. Thus, they are found easily at almost all sampling locations. *Sargassum hemiphyllum* and *Ulva pertus* can be taken both in spring and in autumn, however *Undaria pinnatifida* can be taken only in spring. Each seaweed sample was washed by surrounding seawater to remove attachment at sampling place. In addition, each sample was washed completely by filtered seawater in our laboratory based on Kato et al. (2003).

Seawater samples were also collected from each sampling points. Each seawater sample was filtered through a 0.45 μ m membrane filter immediately after sampling. The basic data of water qualities, such as temperature, pH, EC (electric conductivity), ORP (oxidation-reduction potential) and DO

(dissolved oxygen) for samples were measured by a handy pH/COND and pH/DO Meter (HORIBA, D-24 and D-25) at each sampling point or in the laboratory.

2.2 Analytical Method

2.2.1 Determination of REEs, Th and U in seaweed samples

REEs, Th, and U standard solutions used for making the calibration curve were prepared by diluting the standard solution (XSTC-1 for REEs and XSTC-13 for Th, U; both $10\text{mg} \cdot \text{dm}^{-3}$ 5% HNO_3 solution) purchased from SPEX CertiPrep, Inc. (USA).

Each seaweed sample was ashed at $450\text{ }^\circ\text{C}$ for 48 h. The ash (c.a. 0.5 g) was dissolved with 10 cm^3 HNO_3 and 5 cm^3 solution in a Teflon beaker as adding H_2O_2 . The sampling solution was evaporated to dryness. After that, the residue was dissolved again with 50 cm^3 of $1\text{ mol} \cdot \text{dm}^{-3}$ HNO_3 . The decomposition of seaweed was mainly based on the procedure described by Fu et al. (2000).

In order to verify the accuracy of the method, a certified reference material (IAEA-140 brown seaweed, *Fucus sp.* reported by Coquery et al. (1997)) was analyzed and the result obtained was in good agreement with the certified value (The relative errors were below 10 % for REEs, and 5 % for Th, U).

2.2.2 Determination of REEs, Th, U in seawater samples

REEs, Th, U in seawater samples were separated from matrix by the chelate disk (47φmm) (EmporeTM Sumitomo 3M Co.). In the separation process, the disk was placed in an ordinary disk holder. Each sample was run through the disk after adjusting the pH to 3 by using ammonium acetate (CH₃COONH₄) and nitric acid (HNO₃). Then, REEs, Th, and U on the disk was eluted by 1.5 mol · dm⁻³ nitric acid (20 cm³). The preconcentration of REEs, Th, and U was carried out according to the procedure described by Takaku et al. (2002). It was confirmed that quantitative recovery values for REEs, Th and U in seawater samples were obtained.

After the preconcentration procedure, the concentrations of REEs, Th and U in samples were measured with an ICP-MS (HP4500; Yokogawa Analytical systems, Tokyo). The operating condition of ICP-MS (including the measured isotope) is shown in Table 1.

3. Results and discussion

3.1 The concentration of REEs, Th and U in seaweed samples in Niigata Prefecture

The mean concentrations of REEs, Th and U in all seaweed samples we analyzed in this work are shown in Fig. 2 per phylum along with error bars. From this figure, the definitive difference of the concentration of light REE (LREE) among

phyla (i.e., green algae, red algae, brown algae) was not observed. However, with regard to middle REE (MREE), heavy REE (HREE) and Th, a slight difference was observed. On the other hand, the concentration of U largely varies with the phylum of seaweed. It is evident that, the concentration of U in brown algae is the highest and those in green algae is the lowest.

The high concentration of U in brown algae is attributed to the alginic acid. Alginic acid is constituent of the cell walls of brown algae. It is considered that alginic acid has high adsorptive capability of U (e.g., Seki and Suzuki, 1998; Diniz and Volesky, 2005).

To investigate the biological concentration of the seaweeds (i.e., to investigate of the concentration of REEs, Th and U in seaweeds relative to that in seawater), the concentration of REEs, Th and U in seawater were also determined for reference. The representative results in autumn 2004 are shown in Table 2. The relative standard deviation (RSD) of three replicated analyses were less than 5 % for most data, although for some data were less than 10 %. As shown in this table, the concentrations of U in seawater samples are considerably high. This is due to the stability of uranium oxide ion (UO_2^{2+}) in seawater. Normalized REE concentrations (REE patterns) in seawater samples taken at four different seasons (i.e., spring, summer, autumn and winter) are shown in Fig. 3. The REE

pattern, where the abundance of lanthanide in each sample (relative to that of chondrite meteorite or shale) is plotted on a logarithmic scale against the atomic number, is therefore regarded as a "finger print" of a geological sample (Henderson. P., 1984; Akagi, T. et al., 2004). In this figure, the value of Leedeey (Masuda et al., 1973; Masuda, 1975), one of the chondrite meteorites, was selected because it is considered as the most primitive and represent the mean abundance of elements in the solar-system.

From Fig. 3 and Table 2, it is also found that the concentrations of REEs, Th and U in seawater samples are hardly vary with seasons and/or sampling points. However, only "dissolved" fractions in seawater samples have been analyzed in this work. Furthermore, "suspended" fraction should be also studied. Analytical results for "suspended" fraction may permit us to discuss the effect from surrounding geology. Therefore, we are carrying out the determination of REEs, Th and U in "suspended" fraction left in 0.45 μ m membrane filters.

Normalized REE concentrations in some representative seaweed samples are shown in Fig. 4. For reference, the REE pattern in seawater sample is also shown (these data shown in Fig. 4 are all taken in Sado Island). From this figure, it can be observed that the concentrations of REEs in these seaweed samples are about 10^2 - 10^3 times that of seawater sample concentration; the enrichment factor of REEs is larger in HREE

than LREE. These results indicate that all seaweed samples showed biological concentration to some extent with regard to REEs.

In order to investigate the difference of the concentrations of REEs, Th and U among the phyla in more detail, the representative results of each phylum are shown in Table 3. Within green algae, *Ulva pertusa* was chosen because it was remarkably abundant on the coast of Niigata Prefecture. For the same reason, *Grateloupia elliptica* and *Sargassum hemiphyllum* were selected for red and brown algae, respectively. In here, *Undaria pinatiffida* was also featured because of the highest concentration of U in all seaweed species. From Table 3 (by comparing the measurement result of *Sargassum hemiphyllum* with that of *Undaria pinatiffida*), it is found that the difference of REEs, Th and U concentration among species is large even within the same phylum.

Furthermore, REE patterns in five kinds of “brown algae” samples are shown in Fig. 5. From this figure, the order of the concentrations of REEs is roughly *Dictyota dichotoma* > *Sargassum horneri* > *Sargassum hemiphyllum* > *Ecklonia stolonifer* > *Undaria pinnatifida*. The order is particularly remarkable in MREE – HREE, although REE patterns are not so much different among them.

However, it is noteworthy that the concentration of U is the highest in *Undaria pinatiffida* indicating that elemental

fractionation may occur on seaweeds. This result suggests different uptake methods between REEs and U on seaweed as presented consequently in the next section.

Fairly no significant difference of the concentrations of REEs, Th and U in seaweeds among sampling locations and/or seasons were observed. For instance, regarding *Sargassum hemiphyllum* which were taken on the coast of Sanpoku, Izumozaki, Nou and Takachi, the concentrations of REEs, Th and U in this species did not vary remarkably among sampling points as shown in Table 4, although the values are low in the sample from Izumozaki. In Table 4, RSD of three replicated analyses was also less than 5 % for most data. Moreover, with regard to *Sargassum hemiphyllum* which were taken at two different seasons (i.e. both spring and autumn), no significant difference was observed between spring and autumn seasons.

3.2 Different type of uptake method on seaweeds

It is generally considered that two types of uptake mechanism, the adsorption and the absorption occur in case of the accumulation of materials in seaweeds (e.g., Ishii et al., 1980). However, the detailed mechanism is not necessarily clarified fully, and has been left in the room of the research.

Wytttenbach et al. (1994) pointed out that REEs follow the same uptake and deposition processes as Si, and that REEs are stored as hydroxides, together with the amorphous silica. Fu et

al. (2000) also suggested that seaweeds take in silicate salt as nutriment, and that REEs may have been ingested in seaweeds with silicate salt simultaneously.

On the other hand, it can be considered that high concentration of U in brown algae can be related to the alginic acid in brown algae cell wall (e.g., Sakaguchi, 1992. Seki et al., 1998). U may have been more adsorbed on the substances composing cell wall (e.g. alginic acid) rather than a product of cell metabolism. It is expected that this characteristic of U leads to the definite difference of U concentrations among phyla.

As suggested above section, it can be considered that the uptake method (and/or the behavior) of U is different from that of REEs as judged from the measurement results of seaweed in this work. These results obtained in this work are consistent with the uptake mechanism Wytttenbach et al. (1994) and Zhang et al. (2003) suggested.

However, further investigation of the uptake mechanisms of REEs, Th, U, and other elements on seaweeds is needed. Laboratory-model experiments for the uptake of REE, Th and U into seaweed, we are carrying out, can also contribute the elucidation of the mechanism for the ingestion and accumulation of these elements on seaweed.

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