Journal of Alloys and Compounds 408–412 (2006) 525–528

Journal of
ALLOYS
AND COMPOUNDS

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Concentrations of REEs, Th and U in river waters collected in Japan

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Received 30 July 2004; received in revised form 16 November 2004; accepted 15 December 2004

Abstract

Fifteen major rivers were selected for determination of concentration levels in order to understand behaviors of the rare earth elements (REEs), Th and U in Japanese rivers under normal conditions. Ten samples were collected in each river from the upper stream region to the river mouth and the concentrations in the samples were measured by inductively coupled plasma mass spectrometry (ICP-MS). The geometric mean concentrations of REEs except for La, Ce and Nd in the 15 rivers were <0.5–20 ng L^{-1} (ppt), while those of La, Ce and Nd were at 80–200 ppt. These values are close to those reported previously for Japanese river waters and for average river water. The concentration pattern of REEs followed the Oddo–Harkins rule in each river and the concentration range of each element was usually narrow. The concentration range of U was wider than that of Th, probably because of application of phosphatic fertilizer to agricultural fields near the rivers.

Keywords: Rare earth elements; Surface river water; Distribution; Inductively coupled plasma mass spectrometry

1. Introduction

Lanthanides (atomic numbers $Z=57$–60 and 62–71), members of Group IIA in the periodic table, are known as rare earth elements (REEs) and they have similar physical and chemical properties. The concentrations of La, Ce and Nd are more than 10 mg kg^{-1} in the continental crust (CC) [1], but the others are below several mg kg^{-1} levels. Toxicity of REEs to human beings is not clearly known because their environmental levels are low; however, industrial emissions of REEs to the environment and application of REEs to agricultural fields, especially in China, are increasing [2]. It is necessary to clarify their paths to human beings, although knowledge of their fate in the environment is limited.

Ingestion of foods and water is one of the most important paths by which REEs go to human beings. From this viewpoint, river water is of interest because it can transport REEs from discharge sites to agricultural fields, and it is also used as drinking water. In the Netherlands, lanthanide concentrations in samples collected from the freshwater environments have been measured to understand the fate of REEs in freshwater ecosystems [3,4]. Although concentration levels of REEs, Th and U in river waters collected in Japan have been reported [5], behaviors of these elements along the rivers were not clarified because only one sampling point per river was selected for determination.

In order to understand the background levels of REEs in Japanese rivers under normal conditions and the variation of concentration levels of REEs in waters from the upper stream region to the river mouth, 10 samples were collected from each river and the concentrations were measured with inductively coupled mass spectrometry (ICP-MS). Fifteen major rivers were selected for this purpose. The data were used to calculate annual input of dissolved REEs from the rivers to the sea. Additionally, Th and U concentrations were measured; although these naturally occurring elements are actinides which lie just below lanthanides in the periodic

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doi:10.1016/j.jallcom.2004.12.104

table, their behaviors in the environment are also interesting from a radioecological viewpoint.

2. Experimental

From throughout Japan, 15 major rivers were selected and sampling was carried out for the Abukuma, Naka, Abe, Yodo and Yoshii Rivers in 2002 and for the Ishikari, Tokachi, Mogami, Shinano, Ara, Chikugo Kiso, Kino, Gono and Yoshino Rivers in 2003 as shown in Fig. 1. In order to obtain REEs, Th and U concentrations in water under normal conditions, only 2–3 days were spent in collection at any one river because river conditions can be affected by the weather and the season. Ten samples per river were collected from the upper stream to the river mouth.

At a sampling site, water was collected in two clean-washed polypropylene bottles, and electric conductivity and pH were measured. Water of one bottle (100 mL) was for ICP-MS measurement and that of the other (500 mL) was for weight determination of suspended solid (SS). There, for ICP-MS samples, each water sample was filtered (<0.45 μm) and acidified with 1 mL of concentrated nitric acid (ultra-pure analytical grade AA-100, Tama Chemicals Co., Japan). All sample bottles were sent to the institute laboratory under cool conditions (<5 °C). In the laboratory, the SS amount was obtained after passing the sample through a 0.45-μm Millipore filter and calculating the dry weight differences of the filter before and after the sample passage.

Fig. 1. A map of Japan showing the 15 rivers for sample collection.

The concentrations of dissolved REEs, Th and U in the sample water were directly measured twice by quadrupole ICP-MS (Yokogawa, Agilent 7500a) within 1 month after the collection. However, for high salinity samples, dilutions were made up to 1000 times, depending on their salt content. Standard solutions for ICP-MS were prepared from multi-element standard solutions (XSTC-1 and XSTC-355, SPEX CertiPrep Inc., USA). Detection limit for REEs, Th and U by ICP-MS was around 0.2 pg mL^{-1} (ppt).

3. Results and discussion

The concentrations of REEs, Th and U from the upper to downstream regions are shown in Fig. 2 for the Ishikari, Abukuma, Shinano, Kiso, Kino and Chikugo Rivers. Some results for samples collected near the river mouth were omitted when the influence of seawater was clearly observed. In some samples, several REEs were not determined due to their lower concentrations than detection limits. The REE concentrations from the upper stream to downstream regions usually increased slightly or were almost the same except for the Abukuma and Kiso Rivers, which both had the highest values in the middle stream region. However, the concentration range of each element in all 15 rivers (data for 9 rivers are not shown) was usually narrow. Probably, dissolution and precipitation of REEs were in equilibrium in most river waters.

The geometric mean concentrations of REEs except for La, Ce and Nd in the 15 rivers were <0.5–20 ppt, while those of La, Ce and Nd were at 80–200 ppt. The concentration pattern of REEs followed the Oddo–Harkins rule in each river. The concentrations of the heavier REEs were smaller than those of the lighter REEs. The geometric mean concentrations of Th and U in each river were 2.2–9.4 and 3.3–38 ppt, respectively. The measured concentrations had the same tendencies as previous reported values [5]. The REE concentrations in Japanese rivers are lower than those in the Amazon and Great Whale Rivers, but close to the world average [6]. For each river, geological background, such as rocks, soils, vegetation, river branches and human activities affected the concentration levels. Yamasaki et al. [7] reported U concentrations in Japanese soils, and using their data, we found a regional difference, that is, the U concentration in soil was higher in southwest Japan than in northeast part. This could be explained by differences of bedrocks; granites content in the southwest is higher than in the northeast. In the present study, however, the REEs, Th and U in the river waters that should contact with soils, did not show any regional differences. More data are needed for further discussions.

The geometric mean concentrations of the studied elements were normalized by CC [1]. As shown in Fig. 3, most of the normalized patterns of dissolved REEs showed enrichment for heavy REEs, but some rivers, e.g., Tokachi and Abe, still had a zigzag pattern. The normalized REEs in these rivers

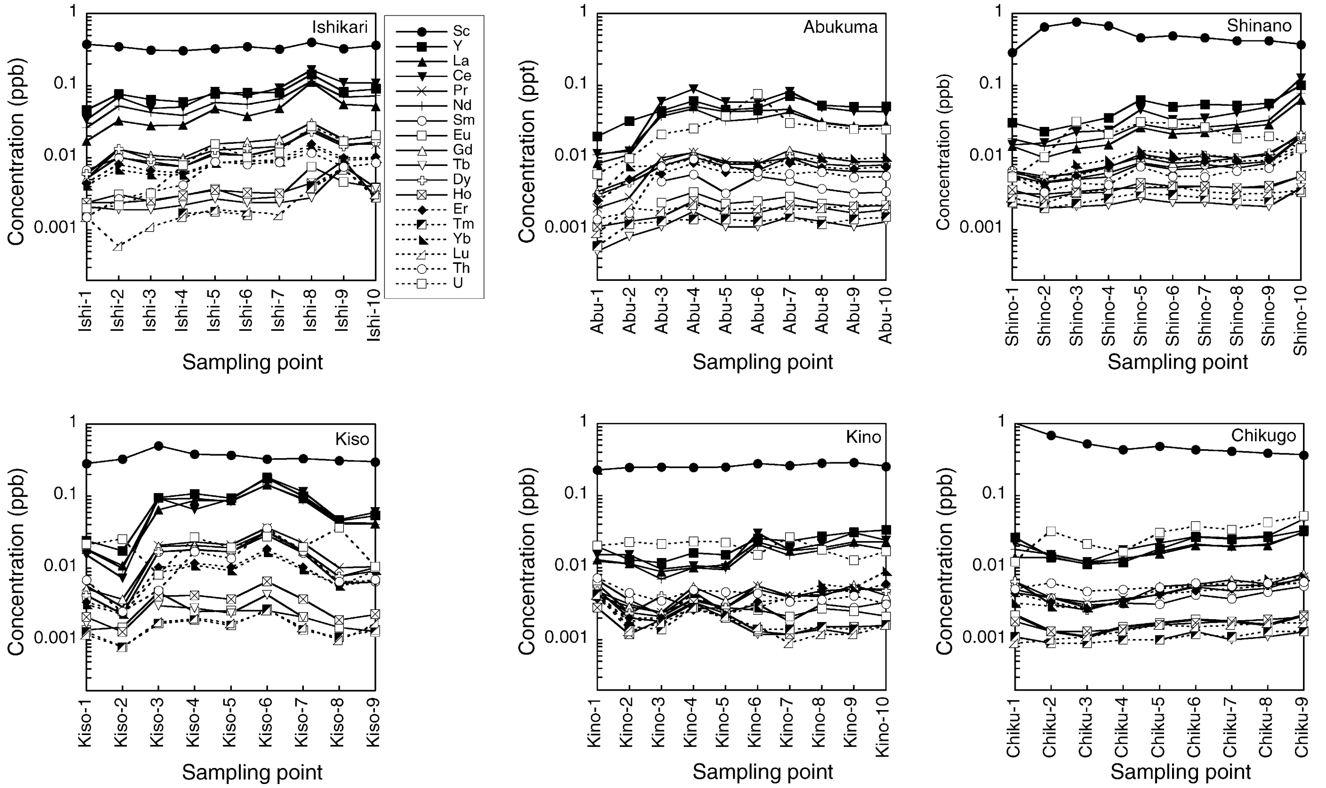

Fig. 2. Concentrations of REEs, Th and U in Ishikari, Abukuma, Shinano, Kiso, Kino and Chikugo Rivers collected in 2002–2003 determined by ICP-MS without preconcentration. Data from sampling points which showed high EC (>1 mS cm^{-1}) were not included.

had positive correlations ($r > 0.3$, $p < 0.05$) with SS and negative correlations ($r < -0.3$, $p < 0.05$) with pH and EC (data not shown). It was reported that the EC and SS affected the concentrations of dissolved REEs in these rivers under neutral pH conditions [8]. In the studied rivers, the EC values were 0.7–2.2 mS cm^{-1} and SS values were 0.9–19 mg L^{-1}. All samples had pH values which ranged from 6.5 to 8.6 and all the rivers had average values which were almost neutral. The SS and pH values were within the order of reported values [9]. Although these properties were measured, the observed behaviors of REEs were difficult to explain for each river from only this one sampling time; more data collected in different years are needed for each river.

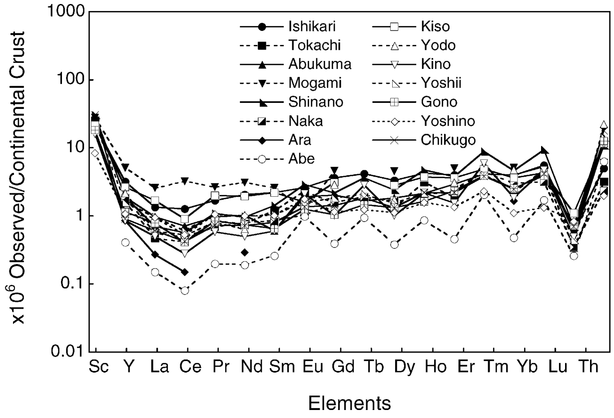

Fig. 3. REEs, Th and U abundance patterns of filtered river waters collected from 15 rivers in Japan normalized to average continental crust ($\times 10^6$).

For Th and U, the concentration ratios of Th/U were 0.10 (min.) and 2.3 (max.) with an average of 0.51; the average value was lower than the ratios in C1 chondrites, 3.6 [10] and in CC, 5 [1]. Similarly, a low Th/U ratio of about 0.15 was reported previously [5]. One reason for the seemingly low value is that U is soluble as UO_2^{2+} and it forms a soluble and stable chelating compound with carbonate, while Th is less soluble forming a colloid with SS including soil particles in the river water. Additionally, phosphatic fertilizer made from phosphogypsum which is known to contain U, was applied to agricultural fields near the rivers so that an excess amount of U would be observed in the water samples.

In order to estimate annual input of dissolved REEs, Th and U from the rivers to the sea under normal conditions, the concentrations of three downstream sampling points of each river were used for the tentative calculation (Table 1). In this calculation, reported average run-off rates for the 15 rivers were used [11]; it was estimated that annual run-off was about 6×10^{10} m^3 in total for the rivers. The calculated amount of REEs that reached the sea was <0.1–2.7 t. These lanthanides are less soluble in the sea due to high salinity [8] so that they are distributed as particles [12].

In summary, the REE concentrations in Japanese rivers are close to the world average, and all of them are at ppt levels.

Table 1
Concentrations of REEs, Th and U at three downstream points in each river and annual inputs of these elements as dissolved forms; results were for 15 Japanese rivers running to the sea and having an average annual water run-off of 6×10^{10} m^3

Element	Concentration at three downstream points ($\mu g\,L^{-1}$)	Annual input to the sea ($t\,y^{-1}$)
Sc	0.35 ± 0.10	21
Y	0.047 ± 0.024	2.8
La	0.028 ± 0.018	1.7
Ce	0.045 ± 0.031	2.7
Pr	0.007 ± 0.005	0.43
Nd	0.031 ± 0.021	1.8
Sm	0.006 ± 0.005	0.39
Eu	0.002 ± 0.001	0.14
Gd	0.009 ± 0.006	0.56
Tb	0.002 ± 0.001	0.1
Dy	0.007 ± 0.004	0.45
Ho	0.002 ± 0.001	0.13
Er	0.006 ± 0.003	0.36
Tm	0.002 ± 0.001	0.1
Yb	0.007 ± 0.003	0.42
Lu	0.002 ± 0.001	0.1
Th	0.005 ± 0.003	0.32
U	0.021 ± 0.014	1.3

Although these concentrations were at ultra-trace levels, they are none the less important because their application in industry are increasing, further study is necessary to understand the REEs, Th and U behaviors in freshwater ecosystems and the long-term effects on the biota, environment and human beings.

Acknowledgements

This work has been partially supported by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade and Industry (METI), Japan.

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