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Gadolinium Anomaly in the Distributions of Rare Earth Elements Observed for Coastal Seawater and River Waters around Nagoya City

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Coastal seawater and river water samples were collected near Nagoya port, located in the coastal area of the Ise Bay, and in six rivers around Nagoya City. The rare earth elements (REEs) in these samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) with chelating resin preconcentration. The concentrations of all REEs except for Pm in coastal seawater and river water samples could be determined at the concentration level from sub-ng L^{-1} to 10 ng L^{-1}. In order to examine the relative concentration variations, the REE patterns were estimated by normalizing the concentrations of REEs in the water samples to those in Post Archean Average Australian Shale (PAAS). Significantly positive Gd anomalies in the REE patterns were observed for river waters down from the urban areas as well as for coastal seawater. Such Gd anomalies were especially remarkable for river water collected near sewage treatment facilities in the Tenpaku river. It was, thus, concluded that the Gd anomalies in the REE patterns were artificially caused by anthropogenic sources mainly due to recent use of a gadolinium compound as a contrast reagent for magnetic resonance imaging (MRI) in medical diagnosis.

Rare earth elements (REEs) ubiquitously distribute in the geochemical samples as well as in the biological samples,[1,2] although their concentrations are generally very low. However, some regularities or characteristics of the concentration distributions of REEs are often found in such samples. Thus, the concentration distributions of REEs in the geological samples are used as the indicator elements to obtain the information about the origins and features of the samples.[3,4] On the other hand, in recent years, REEs have been widely used in functional materials, catalysts, and other products in industry, which have resulted in the emission of REEs into the environment. Under such situations, the concentrations of REEs may be increasing even in natural water, so that REEs are now the notable elements not only in geochemistry but also in environmental chemistry.

So far, the determination of REEs in geochemical and environmental samples has been performed by inductively coupled plasma atomic emission spectrometry (ICP-AES),[5] inductively coupled plasma mass spectrometry (ICP-MS),[2] neutron activation analysis (NAA),[6] and isotope dilution-thermal ionization mass spectrometry (ID-TIMS).[7] Since the concentrations of REEs in natural water are in general extremely low, it is not so easy to determine the accurate concentrations of all REEs in natural water even now. Among the analytical methods mentioned above, ICP-MS has a capability of simultaneous multielement detection with high sensitivity,[2] and thus it has been extensively used for the simultaneous determination of REEs at the low ppt or sub-ppt level in natural water, with the aid of the appropriate preconcentration methods, such as chelating resin preconcentration,[8–11] coprecipitation,[12] and solvent extraction.[13]

It is well known that the concentration distributions of REEs in natural water generally show the zig-zag patterns, according to the rule of Oddo–Harkins,[14] which indicates that the concentrations of REEs with even atomic numbers are higher than those of the neighboring REEs with odd atomic numbers. In geochemistry, thus, the REE patterns, which are obtained by normalizing the concentrations of REEs in the samples to those in chondrite, are often used for considerations on the characteristics of the water samples. However, in the case of natural water, the shale-normalized REE pattern may be preferable to the chondrite-normalized REE pattern because the shales are related to the average concentrations of the elements on the surface of the earth crust. It is also noted here that heavy REEs generally provide the relatively higher concentrations than light REEs[15,16] in such shale-normalized REE patterns for natural water samples.

These days, the positive Gd anomaly, that is, the result that the shale-normalized concentration of Gd is relatively higher than those of the neighboring elements, has been reported for coastal seawaters around Tokyo in Japan[17] as well as those around the urban areas in Germany[18,19] and France.[20] Those reports suggested that such positive Gd anomalies might be artificially caused by anthropogenic sources. In the present study, hence, in order to further ensure the positive Gd anomaly in the REE patterns for river water and coastal seawater samples collected around a big city, the concentrations of REEs in river waters and coastal seawater around Nagoya City were determined by ICP-MS with chelating resin preconcentration.

Experimental

Instruments. An ICP-MS instrument (SPQ8000A; Seiko Instruments, Chiba), equipped with a quadrupole mass spectrometer, was used for the determination of REEs in the water samples. The operating conditions of ICP-MS are summarized in Table 1; these were obtained after optimization procedures of the instrumental

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Table 1. Operating Conditions for ICP-MS

ICP-MS	Seiko Instruments SPQ 8000A
Plasma conditions:	
RF frequency	27.12 MHz
RF power	1.0 kW
Coolant gas flow rate	Ar 16 L min^{-1}
Auxiliary gas flow rate	Ar 1.0 L min^{-1}
Carrier gas flow rate	Ar 1.0 L min^{-1}
Sampling conditions:	
Sampling depth	12 mm from load coil
Sampling cone	Copper, 1.1 mm orifice diameter
Skimmer cone	Copper, 0.35 mm orifice diameter
Nebulizer	Glass concentric type (Meinhard TR-30-C2)
Sample uptake rate	1.0 mL min^{-1}
Data acquisition:	
Scanning mode	Peak hopping
Data points	3 points/peak
Dwell time	10 ms/point
Number of scans	100 times

Table 2. Compositions of Multielement Standard Solutions for the ICP-MS Measurement[a)]

Group	Element	Concentration
Std. 1	Dy, Ho, Er, Tm, Lu	5 ng mL^{-1}
Std. 2	Y, La, Ce, Pr, Nd	25 ng mL^{-1}
	Yb	5 ng mL^{-1}
Std. 3	Sm, Eu, Gd, Tb	5 ng mL^{-1}
Std. 4	Ba	50 ng mL^{-1}

a) Each of the multielement standard solutions for ICP-MS measurement contains Ge, In, Re, and Tl (10 ng mL^{-1} each) as internal standard elements. Std. 4 was used for the correction of spectral interference.

parameters.

A compact Twin pH meter from Horiba (Kyoto) was used for the pH measurements in the chelating resin preconcentration. In the pH measurement, the pH of a small portion (0.1–0.2 mL) separately taken from the sample solution was measured to avoid contamination from electrode materials. The purified water (18.2 MΩ cm) used throughout the present experiment was prepared by a Milli Q SP-TOC system (Nihon Millipore Kogyo, Tokyo).

Chemicals. The standard solutions for making the working calibration curves in the ICP-MS measurements were prepared by mixing the single-element standard stock solutions (1000 mg L^{-1}) for atomic absorption spectrometry, which were purchased from Wako Pure Chemicals (Osaka). The compositions of the multielement standard solutions used for the ICP-MS measurement are shown in Table 2, where the Ba solution was used for interference correction of ^{135}Ba^{16}O with ^{151}Eu. Nitric acid, hydrochloric acid, acetic acid, and aqueous ammonia solution were of electronics industry grade (Kanto Chemicals, Tokyo). Ammonium acetate solution (pH 6) used for pH adjustment was prepared by mixing equivalent molar amounts of acetic acid and ammonia solution.

The chelating resin (Chelex 100 in 100–200 mesh; Bio-Rad Laboratories, CA, USA) was used for preconcentration of REEs in natural water samples.[8–10] The Chelex 100 resin, which has the iminodiacetate functional groups, usually allows one to concentrate divalent and trivalent metal ions unselectively. Before the preconcentration procedure, the chelating resin was cleaned by keeping it in 5 M HCl and changing the acid once everyday for 5 days. After the resin was collected on a G4 glass filter, the resin was further rinsed with 2 M nitric acid and purified water, and kept in a dessicator. The resin thus precleaned was subjected to the preconcentration of REEs in the water samples.

Samples. Coastal seawater samples were collected near Nagoya port, located in the coastal area of northern Ise Bay, in June, 2001. River water samples around Nagoya City were collected from the Tenpaku, Shonai, Kiso, Nagara, and Ibi rivers, which flowed into the Ise Bay, from September to November, 2001. The Tenpaku and Shonai rivers flowed through the urban areas in Nagoya City, while the Kiso, Nagara, and Ibi rivers flowed in the suburb areas outside of Nagoya City. The sampling locations of the rivers described above will be seen later in the related part of discussion.

Furthermore, four samples were collected from the Tenpaku river at different locations from upstream down to estuary. Two samples were also collected at the upstream and midstream areas, respectively, in the Ueda river, which is a tributary of the Tenpaku river. The sewage treatment facilities are located at 5 places down the Tenpaku and Ueda rivers; the locations of the sewage treatment facilities are also shown in Fig. 5. The water sample from the Shonai river was collected at the estuary area. The river water samples from the Kiso, Ibi, and Nagara rivers were collected at the downstream areas, 10 km away from the estuary. All water samples collected were filtered through the membrane filters with pore size of 0.45 µm (Omnipore filter made of PTFE with diameter 47 mm; Millipore, Bedford, MA, USA) immediately after sampling. The dissolved samples filtered with the membrane filters were acidified to pH ca. 1 by adding conc. HNO$_3$. The acidified samples were subjected to chelating resin preconcentration, as described below.

Determination of REEs in the Coastal Seawater and River Water Samples. The chelating resin preconcentration was carried out in a similar manner to that used in previous studies.[8,9] The preconcentration procedure employed in the present experiment was as follows. First, 500 mL of sample solution was taken in a beaker, and then the pH of the solution was adjusted to 6.0 with acetic acid and ammonia solution. Next, 0.3 g of chelating resin (Chelex 100) was added into the solution, and the solution was stirred with a magnetic stirrer for 2 h. The resin was collected on the glass filter (G4; 1.4 cm i.d.) and washed with 10 mL of purified water and 15 mL of 1 M ammonium acetate solution (pH 6) to elute major elements (Ca and Mg) adsorbed on the resin. After further washing the resin with 10 mL of purified water, REEs adsorbed on the resin were eluted with 9 mL of 2 M HNO$_3$ solution, and 1 mL of a mixed solution of In and Re (100 µg L^{-1} each) as the internal standard elements in 2 M HNO$_3$ was added to the concentrated solution. Consequently, the ca. 50-fold preconcentration factor was achieved for the analysis solution in the present procedure, which was subjected to the simultaneous multielement determination of REEs by ICP-MS. In the ICP-MS measurement, the internal standard correction was performed to correct matrix effects due to major elements,[21] because ca. 100 mg L^{-1} of matrix elements (Ca and Mg) as the total still remained in the analysis solution. In addition, the spectral interferences of ^{135}Ba^{16}O^{+} with ^{151}Eu^{+}, ^{141}Pr^{16}O^{+} with ^{157}Gd^{+}, and ^{143}Nd^{16}O^{+} with ^{159}Tb^{+} were corrected in the ICP-MS measurement.[9]

In the recovery test, 5 mL of mixed standard solution containing analyte elements (500 µg L^{-1} each) was added into 500 mL of water sample solution, and the preconcentration procedure de-

Table 3. Analytical Results for the Concentrations of Rare Earth Elements in Coastal Seawater Collected near Nagoya Port in 2001, Determined by ICP-MS after Chelating Resin Preconcentaration

Element	m/z	Concentration[a]		Recovery /%	Blank value[b] /ng L^{-1}		Analytical detection limit /ng L^{-1}	Literature value[c] Nie coast /ng L^{-1}
		Observed /ng L^{-1}	RSD /%					
La	139	6.2 ± 0.09	1.5	92.0	0.03	(4.8)	0.005	6
Ce	140	4.68 ± 0.09	1.9	93.6	n.d.[d]	(—)	0.008	5
Pr	141	0.98 ± 0.02	2.0	94.0	0.01	(1.0)	0.005	1.3
Nd	146	4.3 ± 0.2	4.6	90.8	0.1	(2.3)	0.026	6
Sm	147	1 ± 0.1	10	82.9	0.1	(10)	0.024	1.3
Eu	151	0.18 ± 0.02	11	83.1	0.01	(5.4)	0.008	0.3
Gd	157	2.2 ± 0.1	4.5	83.9	0.1	(4.5)	0.027	1.9
Tb	159	0.28 ± 0.02	7.1	85.0	0.01	(3.6)	0.003	0.4
Dy	163	2.1 ± 0.1	4.7	88.6	n.d.[d]	(—)	0.014	2.4
Ho	165	0.55 ± 0.03	5.4	88.7	0.01	(1.8)	0.003	0.6
Er	166	1.8 ± 0.09	5.0	89.0	0.04	(2.2)	0.009	1.9
Tm	169	0.27 ± 0.03	11	89.5	n.d.[d]	(—)	0.004	0.3
Yb	174	1.7 ± 0.1	5.8	87	n.d.[d]	(—)	0.021	1.7
Lu	175	0.39 ± 0.04	10	89.4	n.d.[d]	(—)	0.003	0.3

a) Mean ± σ (standard deviation), $n = 3$. b) The values in parentheses were the percentages of the blank values for the observed values (%). c) The literature values for coastal seawater from Nie coast in Noto Peninsula, cited from Ref. 22. d) Not detected.

scribed above was carried out to estimate the recovery values. The recovery values for REEs were calculated from the differences between the concentrations of REEs in the sample before and after preconcentration, and then they were used for correction of the observed values.

Results and Discussion

Distributions of REEs in Coastal Seawater and River Water Samples. The analytical results for the concentrations of REEs in coastal seawater collected near Nagoya port are summarized in Table 3, together with the recoveries and the analytical detection limits. The concentrations in Table 3 are shown as the means of three independent experimental values. The concentrations of REEs in coastal seawater collected near Nie coast in Noto Peninsula (Ishikawa Prefecture), a less populated local area, are also shown in Table 3 for comparison. As can be seen in Table 3, the concentrations of REEs in coastal seawater near Nagoya port were in the range from 6.2 ng L^{-1} for La to 0.18 ng L^{-1} for Eu, which were determined with the relative standard derivation (RSD) of 2–10%. In addition, the recoveries for REEs were large (83–94%) enough to obtain reliable analytical data. The analytical detection limits were estimated from the instrumental detection limits, taking into consideration the concentration factors and recovery values. The analytical detection limits of REEs shown in Table 3 were 0.003–0.027 ng L^{-1}, which were low enough to determine REEs in coastal seawater. The observed values for Eu, Gd, and Tb were corrected by using the spectral interference correction coefficient method.[9] The percentages of the corrected concentrations to the observed values were 1.3, 6.2, and 3.3% for Eu, Gd, and Tb, respectively.

According to the literature values[22] shown in Table 3, REEs in the coastal seawater collected near Nie coast in front of the Japan Sea were in the concentration range from 6 ng L^{-1} for La to 0.3 ng L^{-1} for Eu, Tm, and Lu, which were almost the same concentration levels as those in coastal seawater from the Ise Bay. These results indicate that the concentrations of REEs in coastal seawater around the urban area were almost identical to those in coastal seawater around the local area.

The analytical results for the concentrations of REEs as well as major elements in river waters collected at the downstream or estuary area around Nagoya City are summarized in Tables 4 and 5, respectively. As can be seen in Table 5, the concentrations of Na, Mg, Ca, and K in the Shonai and Tenpaku river waters were larger than those in other river water samples. These facts indicate that the river water samples in the Shonai and Tenpaku river collected from estuary area were influenced by seawater. As can be seen in Table 4, the concentrations of REEs in the river water samples were in the range from sub-ng L^{-1} to 10 ng L^{-1} level. The REEs in the downstream water from the Kiso river, which provided the highest concentration levels among the water samples examined in the present experiment, were in the concentration range from 26.8 ng L^{-1} for Ce to 0.6 ng L^{-1} for Eu, while those in estuarine water from the Tenpaku river were in the concentration range from 5.2 ng L^{-1} for Ce to 0.3 ng L^{-1} for Eu and Tb, which were the lowest REE concentrations among the river waters examined in the present experiment. Accordingly, the concentrations of REEs in the downstream water of the Kiso river were about 5-fold higher than those in brackish water collected near the estuarine area of the Tenpaku river.

REE Patterns for Coastal Seawaters. In the following discussion, the REE patterns were examined to compare the relative abundances of REEs in coastal seawaters. Here, the concentration of each REE in the water samples was normalized to that in Post Auchean Average Australian Shale (PAAS).[8] The REE pattern for coastal seawater from the Ise Bay (2001) is shown in Fig. 1, where the REE patterns for coastal seawaters from the Ise Bay and the Japan Sea collected in 1992[8] and 1998,[22] respectively, are also shown.

It is seen in Fig. 1 that all the REE patterns became nearly smooth curves after normalization, in which heavy REEs pro-

Table 4. Anaytical Results for the Concentrations of Rare Earth Elements in River Waters around Nagoya City, Determined by ICP-MS after Chelating Resin Preconcentration

Element	Concentration of REEs[a)]/ng L^{-1}				
	Ibi river	Nagara river	Kiso river	Shonai river	Tenpaku river
La	11.5 ± 0.14	9.7 ± 0.13	20.2 ± 1.08	15.4 ± 0.30	4.2 ± 0.38
Ce	20.8 ± 0.49	13.4 ± 0.33	26.8 ± 1.83	18.2 ± 0.20	5.2 ± 0.39
Pr	3.1 ± 0.09	2.4 ± 0.09	4.9 ± 0.28	3.3 ± 0.10	0.9 ± 0.07
Nd	12.9 ± 0.17	11.3 ± 0.13	19.2 ± 0.97	13.6 ± 0.30	3.9 ± 0.16
Sm	2.8 ± 0.04	2.80 ± 0.20	4.4 ± 0.32	3.3 ± 0.05	1.0 ± 0.04
Eu	0.77 ± 0.00	0.61 ± 0.01	0.6 ± 0.03	0.6 ± 0.03	0.3 ± 0.01
Gd	3.53 ± 0.21	3.87 ± 0.13	5.3 ± 0.20	8.9 ± 0.10	14.0 ± 1.2
Tb	0.45 ± 0.03	0.49 ± 0.01	0.7 ± 0.04	0.8 ± 0.01	0.3 ± 0.04
Dy	2.68 ± 0.16	3.38 ± 0.17	5.0 ± 0.06	7.1 ± 0.20	3.2 ± 0.21
Ho	0.48 ± 0.01	0.79 ± 0.01	1.3 ± 0.05	2.3 ± 0.02	1.1 ± 0.08
Er	1.35 ± 0.04	2.73 ± 0.06	4.5 ± 0.12	9.5 ± 0.10	5.1 ± 0.42
Tm	0.17 ± 0.01	0.45 ± 0.01	0.7 ± 0.06	1.9 ± 0.05	1.0 ± 0.08
Yb	1.22 ± 0.12	3.75 ± 0.08	5.0 ± 0.19	11.7 ± 0.10	8.2 ± 0.68
Lu	0.19 ± 0.01	0.62 ± 0.02	1.1 ± 0.06	3.4 ± 0.10	1.0 ± 0.08

a) Mean ± σ (standard deviation), $n = 3$.

Table 5. Concentrations of Major Elements in River Waters around Nagoya City Determined by ICP-AES and pH

Element	Concentration of major element[a)]/µg L^{-1}				
	Ibi river	Nagara river	Kiso river	Shonai river	Tenpaku river
Na	3.29 ± 0.02	4.69 ± 0.02	15.7 ± 0.09	299 ± 9	1570 ± 50
Mg	1.67 ± 0.01	1.84 ± 0.01	2.26 ± 0.02	36.3 ± 0.1	172 ± 0.6
Ca	9.82 ± 0.06	11.0 ± 0.05	8.82 ± 0.09	35.7 ± 0.3	73 ± 2
K	n.d.[b)]	n.d.[b)]	n.d.[b)]	12.2 ± 0.2	48 ± 1
Si	3.28 ± 0.02	4.07 ± 0.02	4.56 ± 0.05	5.95 ± 0.03	7.8 ± 0.1
pH	7.5	7.8	7.8	7.0	7.5

a) Mean ± σ (standard deviation), $n = 3$. b) Not detected.

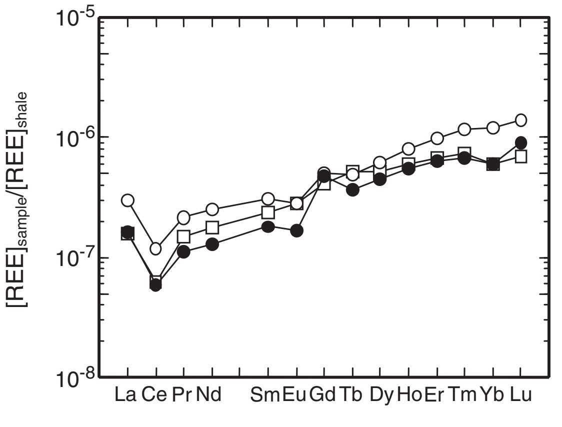

Fig. 1. Shale-normalized REE distribution patterns for coastal seawaters collected form Ise Bay and Japan Sea. ●: Nagoya Port (Ise Bay) in 2001, ○: Nagoya Port in 1992, □: Nie coast (Noto Peninsula; Japan Sea) in 1998.

vided the relatively higher concentrations than light ones. However, it should be noticed here that the negative anomalies of Ce (and Eu) were observed in all the REE patterns for coastal seawaters, and also that the positive anomaly of Gd was clearly observed in the REE pattern for coastal seawater collected near Nagoya port in 2001. REEs usually exist in the oxidation state of +3 with quite similar ionic radii, so that they generally provide the similar chemical properties and behaviors.[14,23] However, Ce(III) is easily oxidized to Ce(IV) in natural water under the aerobic conditions, which is precipitated as Ce(OH)$_4$ and removed from water.[15] Thus, the negative anomaly of Ce is often observed for natural water samples.[7,8]

As is seen in Fig. 1, the positive anomaly of Gd was clearly observed for the coastal seawater from the Ise Bay collected in 2001, while it was slightly observed for coastal seawater from the Ise Bay collected in 1992.[8] On the other hand, such a positive anomaly of Gd was not observed for coastal seawater from the Japan Sea,[22] even though the concentrations of Gd were at almost the same levels in all coastal seawaters examined. The fact that the Gd anomaly was not observed for coastal seawater from the Japan Sea indicate the normal distribution of REEs in seawater around there. On the other hand, the clear Gd anomaly for coastal seawater from the Ise Bay collected in 2001, compared to that in 1992, suggests that the emission of Gd to the aquatic environment has been progressing during last 10 years in the coastal area around Nagoya City. From these experimental results, it was concluded that the Gd anomaly observed for coastal seawater collected from the Ise Bay in 2001 had been caused by the emission from some anthropogenic sources in resent years.

REE Patterns for River Waters. The REE patterns for river waters collected around Nagoya City are shown in Fig. 2. As can be seen in Fig. 2, most river waters except that

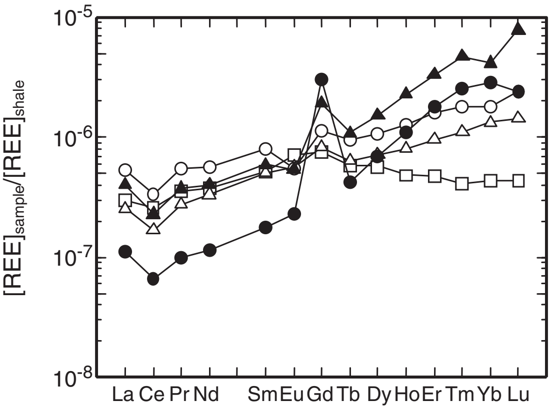

Fig. 2. Shale-normalized REE distribution patterns for river waters around Nagoya City. ○: Kiso river (downstream), △: Nagara river (downstream), □: Ibi river (downstream), ▲: Shonai river (estuary), ●: Tenpaku river (estuary).

from the Ibi river provided the typical REE patterns for natural water, in which the relative concentrations of heavy REEs were higher than those of light REEs. The REE patterns for these river waters were also very similar to those for coastal seawaters shown in the previous section, although the concentration levels of REEs were generally higher in river waters than in coastal seawater. However, it should be noted here that the REE patterns for river waters from the Tenpaku and Shonai rivers provided the larger slopes from light to heavy REEs than those from the Kiso and Nagara rivers. These results may be explained as follows. Since the Tenpaku and Shonai rivers locate around the urban area, the concentrations of dissolved organic substances are relatively high due to eutrophication. It is known that such organic substances form stable dissolved complexes with REEs.[10] In particular, heavy REEs generally have larger complexing abilities with organic substances than light REEs. Thus, it is reasonably considered that the relative abundances of heavy REEs are larger than those of light REEs in the REE patterns for river waters from the urban areas. On the contrary, the Ibi river provided an almost flat REE pattern. Such a flat REE pattern for the Ibi river water may be explained by the fact that REEs in less eutrophicated fresh water exist more as submicron particles or colloids, which pass through a membrane filter with pore size of 0.45 μm.[23] It is known that such submicron particles or colloids contain light REEs more than heavy REEs,[10] which results in the flat REE distribution pattern for less eutrophicated river water.

In Fig. 2, the positive anomalies of Gd were clearly observed for river waters from the Shonai and Tenpaku rivers flowing through the urban areas, but not for those from the Kiso, Nagara, and Ibi rivers in the suburb areas. In particular, the Tenpaku river waters provided the most remarkable Gd anomaly among the rivers investigated. These results suggest that the Gd anomalies in the REE patterns for river waters are caused by some anthropogenic sources.

In order to elucidate the sources of Gd, the REE patterns for the upstream-to-downstream waters from the Tenpaku river (including the Ueda river) were investigated, and the results are shown in Fig. 3. As can be seen in Fig. 3, Gd anomalies were observed significantly for estuarine waters and slightly for midstream waters, although they were hardly observed at all for upstream waters from the Ueda river. These results indicate that Gd was certainly emitted somewhere in the downstream of the Tenpaku river. However, it should be noticed here that the concentrations of Gd in the upstream-to-downstream river waters were at almost the same level. Accordingly, it is difficult to explain this Gd anomaly only from the concentration differences of Gd. In the estuarine area, most of REEs are usually removed, in a similar manner to other heavy metals, as the flocculates of hydroxide colloids, which are more easily formed with the increase in the amounts of salts derived from seawater. However, Gd emitted from anthropogenic sources may be in a stable complex form, which is soluble in water and not much removed by flocculation. Thus, the Gd anomaly in the Tenpaku river was considered to be caused by the increase of Gd in the stable chemical forms.

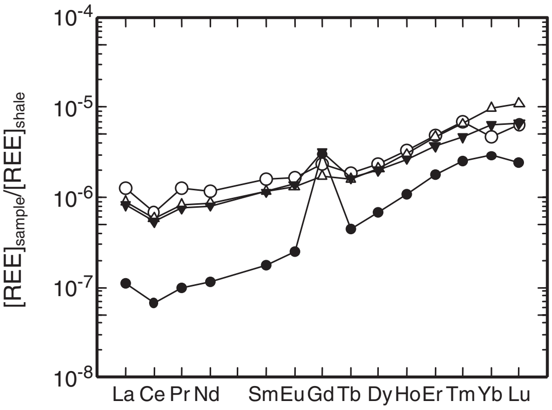

Fig. 3. Shale-normalized REE distribution patterns for Tenpaku and Ueda river waters from upstream to downstream. ○: Ueda river (upstream), △: Ueda river (midstream), ▲: Tenpaku river (midstream), ●: Tenpaku river (estuary).

Estimation of the Degrees of Positive Gd Anomalies. In order to compare the differences of Gd anomalies among the water samples, the positive Gd anomaly in each REE pattern was estimated numerically as the degree (%) of Gd anomaly (P_{anomaly}). Here, P_{anomaly} was conveniently defined by the following equation, as is illustrated in Fig. 4.

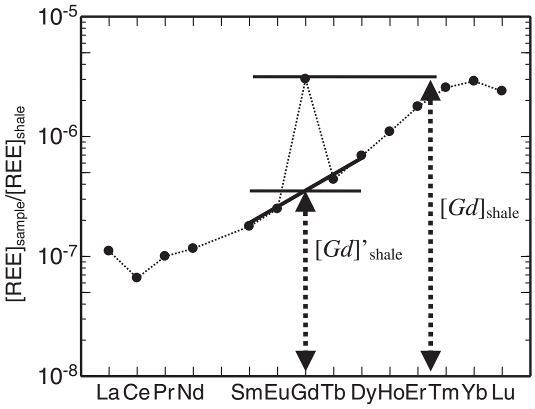

Fig. 4. A scheme for estimation of the degree of Gd anomaly (P_{anomaly}).

$$P_{\text{anomaly}} = \frac{[\text{Gd}]_{\text{shale}} - [\text{Gd}]'_{\text{shale}}}{[\text{Gd}]'_{\text{shale}}} \times 100\ (\%) \qquad (1)$$

where $[\text{Gd}]_{\text{shale}}$ is the shale-normalized concentration of Gd observed in natural water, and $[\text{Gd}]'_{\text{shale}}$ is the normal shale-normalized concentration of Gd when positive Gd anomaly is not observed in the REE patterns at all. As is seen from Fig. 4, $[\text{Gd}]_{\text{shale}}$ was the peak value at the Gd anomaly, and $[\text{Gd}]'_{\text{shale}}$ was approximated from the straight line drawn through the shale-normalized concentrations of Sm, Tb, and Dy. The P_{anomaly} values estimated from the REE patterns for coastal seawater and river waters around Nagoya City are summarized in Table 5, in which the P_{anomaly} values estimated from the literature data[8,9,17,18,24,25] are also shown for comparison, although the filtration conditions of coastal seawater and river waters were different for each study.

In order to compare the Gd anomalies, the P_{anomaly} values for coastal seawater and river waters collected around Nagoya City were plotted on the map in Fig. 5. As can be seen in Fig. 5, the P_{anomaly} values for the downstream waters from the Kiso, Nagara, and Ibi rivers in the suburb areas were 20–40. On the contrary, those for estuarine waters from the Tenpaku and Shonai rivers in the urban areas were 661 and 92, respectively, and they were significantly larger than those for river waters in the suburb areas. It is also seen from Fig. 5 that the P_{anomaly} values for coastal seawater near Nagoya port collected in 2001 was 53.4, which was larger than those for river waters from the Kiso, Nagara, and Ibi rivers, but smaller than those for estuarine waters from the Shonai and Tenpaku rivers. These results certainly indicate that the Gd anomaly for coastal seawater at Nagoya port was caused by the inflow of river water from the urban areas.

In Fig. 5, the P_{anomaly} values for upstream waters from the Tenpaku and Ueda rivers were 42.4 and 12.0, respectively, which indicates that the Gd anomalies were not found in those areas. However, the P_{anomaly} values for the midstream and estuarine waters from the Tenpaku river were 106.3 and 661, respectively. It should be noticed here that five sewage treatment facilities were located down the Tenpaku and Ueda river, as is shown in Fig. 5, and that the significantly large P_{anomaly} values were observed in the midstream water from the Ueda and Tenpaku rivers, located near the sewage treatment facilities. These results suggest that Gd at the high concentration was contained in the drainage water from the sewage treatment facilities, from where Gd were discharged into river water. Thus, it can be stated that the positive Gd anomalies for river waters from the Tenpaku and Ueda rivers were artificially caused by anthropogenic sources. In recent years, $[\text{Gd(DTPA)}]^{2-}$ (diethylenetriaminepentaacetic acid gadolinium(III)) has been used as a contrast reagent for MRI in the hospitals; this is a stable complex soluble in water. Therefore, $[\text{Gd(DTPA)}]^{2-}$ is a possible source compound which causes the Gd anomaly in river water and coastal seawater. The similar possibilities have been pointed out in Tokyo,[17] Germany,[18,19] and France.[20]

Comparison of Positive Gd Anomalies in Seawater and River Waters. The P_{anomaly} values for seawater and river water collected from other areas are also shown in Table 6, which were estimated from the literature data for the distributions of REEs. In the present study, since the filtration of the sample waters was performed by the membrane filter with the pore size of 0.45 µm, the concentrations of light REEs in the dissolved form might be a little high due to colloidal matter that

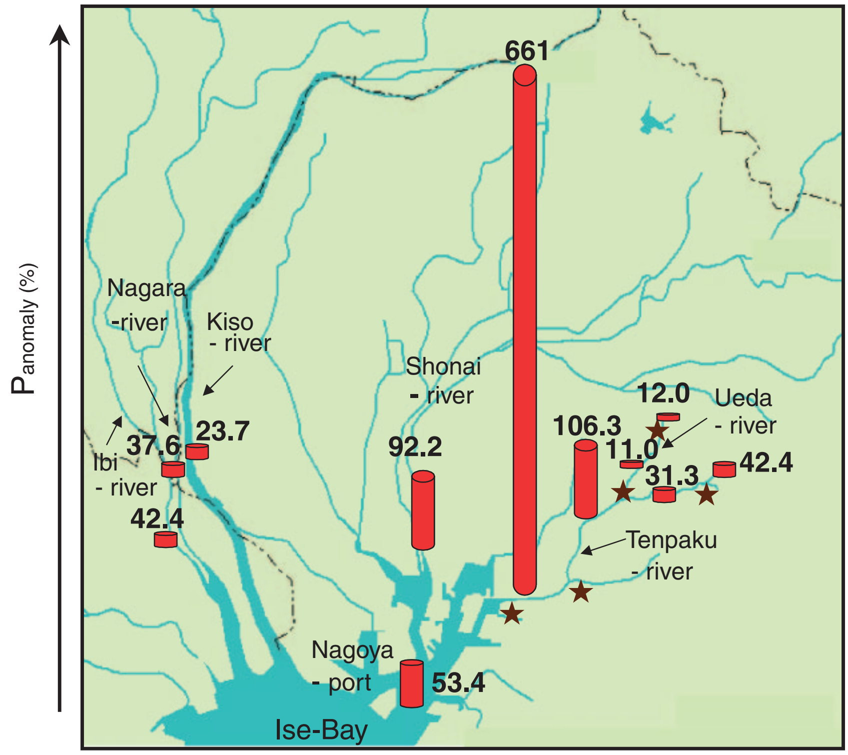

Fig. 5. Comparisons of the degrees of Gd anomalies in coastal seawaters and river waters around Nagoya City. The star marks (★) in the figure indicate the locations of sewage treatment facilities.

Table 6. Comparison of the Degrees of Gd Anomalies (P_{anomaly}) in Coastal Seawater and River Water around Nagoya City and in Other Areas[a)]

Sampling site	Year	$P_{\mathrm{anomaly}}/\%$	Reference
Open seawater			
East-China Sea	1998	1.7	(24)
Antarctic Ocean	1995	14.3	(25)
Offshore seawater			
Ise Bay	1997	23.6	(9)
Osaka Bay	1996	26.1	(24)
Tokyo Bay	1996	95.2	(17)
Coastal seawater			
Ise Bay (Nagoya-port)	**2001**	**53.4**	this work
Ise Bay (Nagoya-port)	1992	11.7	(8)
Japan Sea (Nie coast, Noto)	1998	2.9	(22)
Tokyo Bay (Odaiba)	1996	296	(17)
Upstream river water			
Kiso river	**2001**	**13.3**	this work
Ueda river	**2001**	**12.0**	this work
Downstream river or estuarine water			
Kiso	**2001**	**23.7**	this work
Nagara	**2001**	**37.6**	this work
Ibi	**2001**	**37.8**	this work
Shonai	**2001**	**92.2**	this work
Tempaku	**2001**	**661**	this work
Tone	1996	37.3	(17)
Arakawa	1996	103.5	(17)
Tama	1996	153.8	(17)
River water in foreign countries			
Rhine (Germany)	1995	167	(18)
Havel (Germany)	1995	12140	(18)
Wupper (Germany)	1995	2900	(18)

a) The sampling sites and data written in bold letters were examined in the present study, and the others were done in the literatures cited.

remained in the filtrates. Accrodingly, the Gd anomalies in the present study would be observed to be rather smaller than those in the case of other filtration conditions using the membrane filters with pore size of 0.22 µm or 0.04 µm.

It is seen from Table 6 that the P_{anomaly} values for the East China Sea and the Antarctic Ocean were below 15, which indicates no positive Gd anomalies in these open sea areas. In addition, the P_{anomaly} value for coastal seawater from the Japan Sea (Nie coast) was very low (2.9). This result also indicates that there was no anthropogenic pollution due to Gd in the coastal area of Noto Peninsula. On the contrary, the P_{anomaly} value for coastal seawater from the Ise Bay (2001) was 53.4, which apparently shows the positive Gd anomaly for coastal seawater near the urban area. From the literature values reported by Nozaki et al.,[17] the P_{anomaly} value for coastal seawater from the Tokyo Bay was estimated to be 296, which was about 6-times larger than that for coastal seawater from the Ise Bay. Furthermore, the P_{anomaly} value for off-shore seawater from the Tokyo Bay was 95.2, although those from the Ise Bay and Osaka Bay were below 30. These results for off-shore seawaters in the Tokyo Bay suggest markedly serious progress of the positive Gd anomaly. Thus, it is appreciated from these results that the positive Gd anomalies for coastal seawater are more significantly occurring around a big city with a larger population.

It is also seen in Table 6 that the P_{anomaly} values for estuarine waters from the Arakawa and Tama rivers around Tokyo were 103.5 and 153.8, respectively, which showed the remarkably positive Gd anomalies. However, these P_{anomaly} values observed in the estuarine areas in the Arakawa and Tama rivers around Tokyo were much smaller than that for estuarine water from the Tenpaku river around Nagoya City. As mentioned earlier, the estuarine water from the Tenpaku river, which provided the significantly large P_{anomaly} value, was collected near a sewage treatment facility. These results suggest that the sampling locations for river water should be taken into consideration, when the Gd anomaly in natural water is discussed.

Bau et al. reported the Gd anomalies for river waters from the Havel and Wupper rivers in Germany,[18] and their P_{anomaly} values were estimated to be 12140 and 2900 from their data. The Gd anomalies for river waters in Germany were substantially larger than those for the rivers in Japan. In addition, the remarkable positive Gd anomalies were also reported for some river waters in France,[20] although they are not shown in Table 6. Therefore, it can be stated here that the Gd anomalies have been progressing in the aquatic environment around the urban areas with large human populations all over the world.

Conclusion

The positive Gd anomalies in the distribution REE patterns were observed for coastal seawater and river waters around Nagoya City with more than 2000000 population, while they were not observed for coastal seawater from the Japan Sea as well as for river waters from the local areas. It should be stressed here that such positive Gd anomalies were especially remarkable in the river waters collected near the sewage treatment facilities in the Ueda and Tenpaku rivers. Therefore, it is reasonable to consider that an anthropogenic compound of Gd contained in drainage waters from the sewage treatment facilities is discharged into river water, which is not removed by the activated sludge treatment. A possible chemical species of Gd which provides the Gd anomaly in river water and coastal seawater is $[\mathrm{Gd(DTPA)}]^{2-}$, which is widely used as a contrast reagent for MRI diagnosis in the hospitals. The detection of $[\mathrm{Gd(DTPA)}]^{2-}$ in river water and coastal seawater has not been reported so far, and thus it is really desirable to perform chemical speciation and fate analysis of Gd species in natural water in future.

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