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Fractional Distributions of Trace Metals in Surface Water of Lake Biwa as Studied by Ultrafiltration and ICP-MS

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The distributions of 33 trace metals in the total dissolved fraction (TDF), small molecular weight fraction (SMWF; <10000 Da), and large molecular weight fraction (LMWF; >10000 Da) of surface water from two sampling stations (No. 1 and No. 2) in Lake Biwa (Japan) were investigated. In the experiment, the concentrations of trace metals in TDF and SMWF were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a laboratory-made chelating resin-packed minicolumn for the preconcentration of trace metals. The concentrations of trace metals in LMWF were calculated by subtracting those in SMWF from those in TDF. The comparison between the distributions of trace metals in each fraction collected from the sampling stations No. 1 and No. 2 was made, and the enrichment factors of trace metals in LMWF were estimated. As a result, it was found that soluble biogenic large molecule–metal complexes and hydrogenic particulates were predominantly distributed in LMWF of surface water from Lake Biwa. Furthermore, positive anomalies of Ce and Gd were observed in the shale-normalized rare earth element (REE) distribution patterns.

The toxicities and bioavailabilities of trace metals in natural water depend not only on their total concentrations, but also on their distributions of various species as well as on their chemical forms.[1–4] Consequently, chemical speciation analysis of trace metals in natural water has been extensively performed in the last decade to understand their bio-geochemical behaviors as well as to assess their biological impacts on the environment.[5–13] Recently, the distributions of trace metals in the fractions of dissolved particulate matters (commonly classified by particulate sizes or molecular weights) have attracted great attention,[12–14] because such fractions often contain dissolved organic matter (DOM). Since the concentrations of large organic molecules as well as trace metals in the DOM fraction of natural water were in general at the ppb ($\mu g\,L^{-1}$) or sub-ppb level, such a fraction was usually preconcentrated by ultrafiltration for analysis.[14–19]

Lake Biwa is the largest lake in Japan, where research on trace metal contents, isotopes, and pesticide residues has been conducted to investigate their kinetic behaviors,[20–23] but the fractional distributions of trace metals in Lake Biwa had not yet been investigated in detail. In water quality analysis, the water sample is generally filtered with a membrane filter (pore size 0.45 μm), and the filtrate is referred to as total dissolved fraction (TDF).[23,24] Then, we can obtain the small molecular weight fraction (SMWF) and the large molecular weight fraction (LMWF) from TDF by applying an ultrafiltration technique, where an ultrafiltration (UF) filter with molecular permeation limit of 10000 Da is usually used for preconcentration of large organic molecules.[14–19] SMWF and LMWF obtained by the above procedure are the filtrate passed through the UF filter and the residual solution remained above the UF filter, respectively. In the present experiment, thus, surface water collected from Lake Biwa was fractionated by membrane-filtration and ultrafiltration in order to elucidate the relative distributions of trace metals in the fractions of TDF, LMWF, and SMWF.

Experimental

Water Samples. The surface water samples were collected near the shore at two sampling stations on December, 2002; No. 1 near Hikone City in northern Lake Biwa and No. 2 near Otsu City in southern Lake Biwa. The samples were taken by using a cleaned plastic bucket and stored in 10 L cleaned polyethylene tanks, where the bucket and tanks were cleaned by soaking them in 6 M HNO_3 for one week, followed by rinsing with pure water. The water samples were filtered first with a membrane filter (pore size 0.45 μm; HVLP04700 from Nihon Millipore Kogyo, Tokyo, Japan) immediately after returning to the laboratory. The filtrate obtained here is hereafter referred to as TDF. One liter of the membrane-filtered solution (TDF) was preconcentrated 2-fold with a PELLICON-2 cassette ultrafiltration system (Millipore, Bedford, MA, USA) equipped with a PELLICON-2 UF filter (molecular weight permeation limit 10000 Da) to obtain 500 mL each of SMWF and LMWF. The residual TDF and SMWF solutions were acidified to pH ca. 1 by adding concd nitric acid for preservation. The concentrations of trace metals in LMWF were calculated by subtracting the concentrations in SMWF from those in TDF.

Instruments. An ICP-MS (inductively coupled plasma mass spectrometry) instrument (Agilent HP4500, Yokogawa, Tokyo, Japan) was used for the determination of trace metals, which consisted of a quadrupole mass spectrometer. The ICP-MS instrument

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Table 1. Operating Conditions for ICP-MS Instrument

ICP-MS	Agilent HP4500
Plasma conditions:	
Incident power	1.3 kW
Coolant gas flow rate	Ar 15.0 $\mathrm{L\,min^{-1}}$
Auxiliary gas flow rate	Ar 1.0 $\mathrm{L\,min^{-1}}$
Carrier gas flow rate	Ar 1.0 $\mathrm{L\,min^{-1}}$
Sampling depth	5.5 mm from load coil
Nebulizer:	Micro-mist type
Sample uptake rate	0.1 $\mathrm{mL\,min^{-1}}$
Data acquisition:	
Measurement mode	Peak hopping
Dwell time	50 ms/point
Data point	3 points/peak
Number of scan	100

was equipped with a Micro-Mist nebulizer, with which ca. 0.2 mL of analysis solution was enough for a 2-min measurement. The operating conditions for the ICP-MS instrument are shown in Table 1, which were optimized for better instrument operation.

Chemicals. Nitric acid, acetic acid, and aqueous ammonia solution of electronics industry grade were purchased from Kanto Chemicals (Tokyo, Japan). The multi-element standard solutions for making the working calibration curves were prepared from the single-element standard stock solutions (1000 $\mathrm{mg\,L^{-1}}$) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). The compositions of the multi-element standard solutions are summarized in Table 2. The Chelex 100 resin in 200–400 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). Before the preconcentration procedure, the chelating resin was cleaned by keeping it in 5 M HCl and changing the acid once every day for 5 days. Then, the resin was collected on a G4 glass filter, and it was rinsed with 2 M nitric acid and pure water. The resin was kept in 0.1 M of ammonium acetate at pH 6.0 before use. Pure water used throughout the present experiment was prepared by a Milli-Q purification system (Element A-10, Nihon Millipore Kogyo, Tokyo, Japan).

Preconcentration and Determination of Trace Metals. The concentrations of trace metals in the fractions of TDF and SMWF were determined by ICP-MS. Some of the trace metals could be determined by direct sample introduction, as indicated in Tables 3 and 4, but the concentrations of most trace metals in those fractions were too low to determine without preconcentration. In the present experiment, thus, a laboratory-made chelating resin-packed minicolumn[25,26] was used for the preconcentration of Al, Zn, Cu, Ni, Cd, Ti, Ga, Co, Y, U, and rare earth elements (REEs) before their determination. The minicolumn was constructed with two syringe filters (DISMIC 13HP and Millex-LH) and 0.088 ± 0.004 g ($n = 10$) of chelating resin (Chelex 100, 200–400 mesh) in wet weight, as in a similar manner to that described elsewhere.[25,26]

The preconcentration procedure for trace metals in the fractionated samples was as follows. First, 50 mL of each fractionated sample (TDF or SMWF) was adjusted to pH 6.0 with ammonia solution and acetic acid, and then loaded into the minicolumn at the flow rate of 1.0 $\mathrm{mL\,min^{-1}}$ with a 50 mL volume syringe. Next, 3 mL of 0.1 M ammonium acetate buffer (pH 6.0) and 5 mL of pure water were successively injected at the flow rate of 2 $\mathrm{mL\,min^{-1}}$ for rinsing to minimize the amounts of matrix elements, such as Mg and Ca, adsorbed on the resin. Then, trace metals adsorbed on the chelating resin were eluted with 0.45 mL of 2 M HNO_3 in a 5 mL test tube, into which 0.05 mL of internal standard solution (Ge, In, Re, and Tl 100 $\mathrm{\mu g\,L^{-1}}$ each) was added for the correction of matrix effects in the ICP-MS measurement. As a result, the concentration factor of 100 was obtained for the final analysis solution, which was subjected to the determination of trace metals by ICP-MS equipped with a Micro-Mist nebulizer. In the recovery test, trace metals (from 0.1 $\mathrm{\mu g\,L^{-1}}$ of REEs to 10 $\mathrm{\mu g\,L^{-1}}$ of Ni and Zn) were spiked in the original lake water sample, taking into consideration their concentrations in the sample, and the same preconcentration procedure described above was carried out to estimate the recoveries for trace metals.

Table 2. Compositions of Standard Solutions for Simultaneous Multi-Element Determination by ICP-MS Instrument[a)]

Group	Element	Concentration/$\mathrm{\mu g\,L^{-1}}$
Std. 1	Al, Ti, V, Co, Pb, Ga	50
	Dy, Ho, Er, Tm, Lu	5
Std. 2	Cu, Zn, Cd	50
	La, Ce, Pr, Nd, Yb	5
Std. 3	Mn, Mo	50
	Y, Sm, Eu, Gd, Tb, U	5
Std. 4	Sb	10
Std. 5	Na, K	10000
Std. 6	Mg	10000
Std. 7	Ca	50000
Std. 8	Ba	50000

a) Each of the multi-element standard solutions contains Ge, In, Re, and Tl (10 $\mathrm{\mu g\,L^{-1}}$ each) as internal standard elements.

Results and Discussion

Analytical Figures of Merit. The recoveries, blank values, and analytical detection limits obtained by the present preconcentration and determination methods for trace metals were estimated as in a similar manner to those performed in previous works.[25,26] Since such analytical figures of merit contain almost the same levels or values obtained in a previous work,[26] only the analytical detection limits are shown in the last column of Table 3 for reference. The analytical detection limits for most trace metals in Table 3 were obtained after preconcentration, which were calculated from the instrumental detection limits, taking into consideration the recoveries and concentration factor (100). The instrumental detection limits of trace metals were defined as the concentrations corresponding to 3 times the standard deviation of the background signal intensities, which were estimated from the 10-times duplicate measurements of the blank solution, i.e. 2 M nitric acid with internal standard elements (Ge, In, Re, and Tl 10 $\mathrm{\mu g\,L^{-1}}$ each). In addition, it is noted here that the recoveries for all trace metals were larger than 80%, with standard deviations less than 4%,[26] which seemed to be good repeatability for obtaining reliable results for these metals. The blank signals were observed for Al, Zn, Cu, Ni, Co, Y, Ce, and La, but most of them were negligibly small compared to their concentrations in the fractionated samples investigated in the present work.

The validation of the present analytical method was ensured by the determination of trace metals in a river water certified

Table 3. Concentrations of Trace Metals in Different Fractions of Surface Water Collected at Sampling Station No. 1 in Lake Biwa[a]

Element	m/z	Concentration[b] /μg L^{-1} TDF	SMWF	LMWF	Analytical detection limit[e] /μg L^{-1}
Ca[c]	43	31900 ± 500	31900 ± 400	∼0[d]	12[f]
Na[c]	23	8800 ± 500	9000 ± 200	∼0[d]	0.6[f]
Mg[c]	24	2700 ± 100	2800 ± 90	∼0[d]	0.2[f]
K[c]	39	1640 ± 30	1660 ± 40	∼0[d]	6[f]
Al[c]	27	1.5 ± 0.1	0.79 ± 0.07	0.7 ± 0.2	0.001
Fe[c]	57	86 ± 6	76 ± 3	10 ± 9	8[f]
Zn	66	1.39 ± 0.08	1.33 ± 0.02	0.06 ± 0.10	0.0011
Cu	63	0.53 ± 0.02	0.073 ± 0.002	0.457 ± 0.022	0.00013
Ni	60	0.183 ± 0.006	0.145 ± 0.003	0.038 ± 0.009	0.0014
Mn[c]	55	12.3 ± 0.2	11.0 ± 0.3	1.3 ± 0.5	0.2[f]
V[c]	51	0.371 ± 0.009	0.31 ± 0.01	0.061 ± 0.019	0.012[f]
Cd	111	0.0077 ± 0.0007	0.0059 ± 0.0008	0.0018 ± 0.0015	0.00043
Ba[c]	135	7.9 ± 0.2	7.7 ± 0.3	0.2 ± 0.5	0.048[f]
Ti	47	0.0439 ± 0.0009	0.015 ± 0.001	0.0289 ± 0.0019	0.01
Ga	71	0.0047 ± 0.0003	0.0037 ± 0.0002	0.0010 ± 0.0005	0.024
Sb[c]	121	0.057 ± 0.006	0.059 ± 0.003	∼0[d]	0.00005
Co	59	0.026 ± 0.002	0.0168 ± 0.0008	0.0092 ± 0.0028	0.00004
Y	89	0.0152 ± 0.0006	0.0058 ± 0.0001	0.0094 ± 0.0007	0.00003
U	238	0.143 ± 0.004	0.122 ± 0.003	0.021 ± 0.007	0.00003
Nd	143	0.0028 ± 0.0001	0.00043 ± 0.00008	0.00237 ± 0.00018	0.00009
Ce	140	0.0078 ± 0.0003	0.00155 ± 0.00006	0.00625 ± 0.00036	0.00002
La	139	0.0030 ± 0.0001	0.00045 ± 0.00002	0.00255 ± 0.00012	0.00001
Yb	172	0.0044 ± 0.0003	0.0014 ± 0.0002	0.0030 ± 0.0005	0.00003
Dy	163	0.0017 ± 0.0001	0.00049 ± 0.00009	0.00121 ± 0.00019	0.00005
Gd	157	0.0012 ± 0.0001	0.00044 ± 0.00005	0.00076 ± 0.00015	0.00006
Er	166	0.0025 ± 0.0002	0.0007 ± 0.0001	0.0018 ± 0.0003	0.00004
Sm	147	0.00081 ± 0.00009	0.00019 ± 0.00007	0.00062 ± 0.00016	0.00004
Pr	141	0.00061 ± 0.00002	0.000094 ± 0.000004	0.000516 ± 0.000024	0.00001
Lu	175	0.00117 ± 0.00005	0.00038 ± 0.00002	0.00079 ± 0.00007	0.00001
Ho	165	0.00055 ± 0.00005	0.00015 ± 0.00002	0.00040 ± 0.00007	0.00001
Eu	153	0.000164 ± 0.000006	0.000051 ± 0.000007	0.000113 ± 0.000013	0.00001
Tm	169	0.00053 ± 0.00002	0.00018 ± 0.00002	0.00035 ± 0.00004	0.00001
Tb	159	0.00017 ± 0.00002	0.00004 ± 0.00002	0.00013 ± 0.00004	0.00001

a) TDF: total dissolved fraction, SMWF: small molecular weight fraction, LMWF: large molecular weight fraction. b) Mean ± standard deviation, $n = 5$. c) Determined directly without preconcentration. d) Not available because their concentrations in TDFs were almost the same as those in SMWF. e) Cited from Ref. 25. f) Detection limit without preconcentration.

reference material (JSAC 0301-1, issued by the Japan Society for Analytical Chemistry), as reported in a previous paper.[26]

Analytical Results for the Concentrations of Trace Metals in Fractionated Samples of Surface Water from Lake Biwa. The present analytical method was applied to the determination of trace metals in the fractionated samples (TDFs and SMWFs) of surface water from Lake Biwa. As a result, the concentrations for 33 trace metals were obtained in those fractionated samples. The results for trace metals in TDFs and SMWFs of surface water from stations No. 1 and No. 2 were summarized in Table 3 and Table 4, respectively. It is seen in Table 3 that the concentrations of trace metals in TDF for station No. 1 were in the range from 0.00016 ± 0.000006 μg L^{-1} for Eu to 31900 ± 500 μg L^{-1} for Ca, while those in SMWF were in the range from 0.00004 ± 0.00002 μg L^{-1} for Tb to 31900 ± 400 μg L^{-1} for Ca. It is also seen in Table 4 that the concentrations of trace metals in TDFs for station No. 2 were in the range from 0.00039 ± 0.00003 μg L^{-1} for Eu to 11900 ± 100 μg L^{-1} for Ca, while those for SMWF were in the range from 0.00007 ± 0.00001 μg L^{-1} for Eu to 11400 ± 400 μg L^{-1} for Ca.

The concentrations of trace metals in LMWFs were calculated by subtracting those in SMWFs from those in TDFs, and the results are also given in Tables 3 and 4. The calculated concentrations of trace metals in LMWFs will be used for the following discussion on the fractional distributions.

Fractional Distributions of Trace Metals in Surface Water. Based on the results described above, the fractional distribution factors of trace metals in dissolved fractions, i.e., SMWF and LMWF, were estimated according to the following equations:

$$F_{\mathrm{SMWF}} = [\mathrm{M}]_{\mathrm{SMWF}}/[\mathrm{M}]_{\mathrm{TDF}} \times 100\%, \qquad (1)$$

$$F_{\mathrm{LMWF}} = [\mathrm{M}]_{\mathrm{LMWF}}/[\mathrm{M}]_{\mathrm{TDF}} \times 100\%, \qquad (2)$$

Table 4. Concentrations of Trace Metals in Different Fractions of Surface Water Collected at Sampling Station No. 2 in Lake Biwa$^{\rm a)}$

Element	m/z	Concentration$^{\rm b)}$/μg L^{-1}		
		TDF	SMWF	LMWF
Ca$^{\rm c)}$	43	11900 ± 100	11400 ± 400	500 ± 500
Na$^{\rm c)}$	23	8200 ± 200	8400 ± 500	~0$^{\rm d)}$
Mg$^{\rm c)}$	24	1640 ± 40	1900 ± 100	~0$^{\rm d)}$
K$^{\rm c)}$	39	2480 ± 40	2400 ± 30	80 ± 70
Al$^{\rm c)}$	27	2.9 ± 0.1	0.87 ± 0.08	2.0 ± 0.2
Fe$^{\rm c)}$	57	28 ± 2	24 ± 2	4 ± 4
Zn	66	0.64 ± 0.02	0.65 ± 0.01	~0$^{\rm d)}$
Cu	63	0.408 ± 0.007	0.238 ± 0.006	0.17 ± 0.013
Ni	60	0.354 ± 0.006	0.318 ± 0.004	0.036 ± 0.010
Mn$^{\rm c)}$	55	0.53 ± 0.02	0.5 ± 0.1	~0$^{\rm d)}$
V$^{\rm c)}$	51	0.062 ± 0.007	0.0417 ± 0.0006	0.0203 ± 0.0076
Cd	111	0.0038 ± 0.0002	0.0019 ± 0.0002	0.0019 ± 0.0004
Ba$^{\rm c)}$	135	8.8 ± 0.2	8.0 ± 0.5	0.8 ± 0.7
Ti	47	0.037 ± 0.001	0.0113 ± 0.0006	0.0257 ± 0.0016
Sb$^{\rm c)}$	121	0.15 ± 0.01	0.11 ± 0.01	0.04 ± 0.02
Ga	71	0.0041 ± 0.0001	0.0018 ± 0.0001	0.0023 ± 0.0002
Co	59	0.0069 ± 0.0001	0.0046 ± 0.0009	0.0023 ± 0.001
Y	89	0.0202 ± 0.0002	0.00741 ± 0.00009	0.01279 ± 0.00029
U	238	0.0389 ± 0.0003	0.025 ± 0.001	0.0139 ± 0.0013
Nd	143	0.0111 ± 0.0002	0.0015 ± 0.0001	0.0096 ± 0.0003
Ce	140	0.0321 ± 0.0005	0.00454 ± 0.00008	0.02756 ± 0.00058
La	139	0.0127 ± 0.0002	0.00164 ± 0.00003	0.01106 ± 0.00023
Yb	172	0.0042 ± 0.0001	0.00206 ± 0.00005	0.00214 ± 0.00015
Dy	163	0.0029 ± 0.0001	0.00084 ± 0.00007	0.00206 ± 0.00017
Gd	157	0.0031 ± 0.0001	0.00082 ± 0.00005	0.00228 ± 0.00015
Er	166	0.00249 ± 0.00004	0.00101 ± 0.00007	0.00148 ± 0.00011
Sm	147	0.0025 ± 0.0001	0.00038 ± 0.00002	0.00212 ± 0.00012
Pr	141	0.00284 ± 0.00004	0.00035 ± 0.00001	0.00249 ± 0.00005
Lu	175	0.00094 ± 0.00001	0.00050 ± 0.00003	0.00044 ± 0.00004
Ho	165	0.00068 ± 0.00002	0.00023 ± 0.00002	0.00045 ± 0.00004
Eu	153	0.00039 ± 0.00003	0.00007 ± 0.00001	0.00032 ± 0.00004
Tm	169	0.00046 ± 0.00003	0.00020 ± 0.00002	0.00026 ± 0.00005
Tb	159	0.00040 ± 0.00003	0.00010 ± 0.00001	0.00030 ± 0.00004

a) TDF: total dissolved fraction, SMWF: small molecular weight fraction, LMWF: large molecular weight fraction. b) Mean ± standard deviation, $n = 5$. c) Determined directly without preconcentration. d) Not available because their concentrations in TDFs were almost the same as those in SMWF.

where $F_{\rm SMWF}$ and $F_{\rm LMWF}$ are the fractional distribution factors of trace metals in SMWF and LMWF, respectively, and $[{\rm M}]_{\rm SMWF}$, $[{\rm M}]_{\rm LMWF}$, and $[{\rm M}]_{\rm TDF}$ are the concentrations of trace metals in SMWF, LMWF, and TDF, respectively, which are summarized in Tables 3 and 4. According to the above definition, of course, the sum of $F_{\rm SMWF}$ and $F_{\rm LMWF}$ is supposed to be 100%. The fractional distribution factors of trace metals in the dissolved fractions (SMWF and LMWF) for stations No. 1 and No. 2 are illustrated in Fig. 1a and Fig. 1b, respectively. It is seen from Fig. 1 that Ca, Na, Mg, K, and Sb at station No. 1 and Na, Mg, Zn, and Mn at the station No. 2 existed only in SMWF, while other trace metals existed both in SMWF and in LMWF.

As is seen in Fig. 1, most of the trace metals showed quite complicated distributions between SMWF and LMWF of surface water collected at stations No. 1 and No. 2. Thus, the characteristics of these distributions will be considered by estimating the enrichment factors and relative REE distribution patterns in the following sections. However, it is simply stated here that the large distribution factors of Na, K, Ca, Mg, and Sb in SMWF may be attributed to the fact that they are generally in the ionic forms and easily soluble in water.[15] On the other hand, the $F_{\rm LMWF}$ values for REEs at the two stations were larger than 40%, and, in particular at station No. 2, light REEs provided much larger $F_{\rm LMWF}$ values than heavy REEs. It is known that the distributions of light REEs are generally much larger in rocks and minerals than those of heavy REEs.[27,28] Therefore, the relatively large distributions of light REEs in LMWF at station No. 2 suggest that fine particulates that originated from rocks and/or minerals were contained more in LMWF from No. 2 than in LMWF from No. 1. Further discussion about the distributions of REEs will be given in the following sections.

Concentration Mechanisms of Trace Metals in LMWFs. In order to evaluate the abundance of trace metals in solid samples such as sediment and suspended particulate matter, the

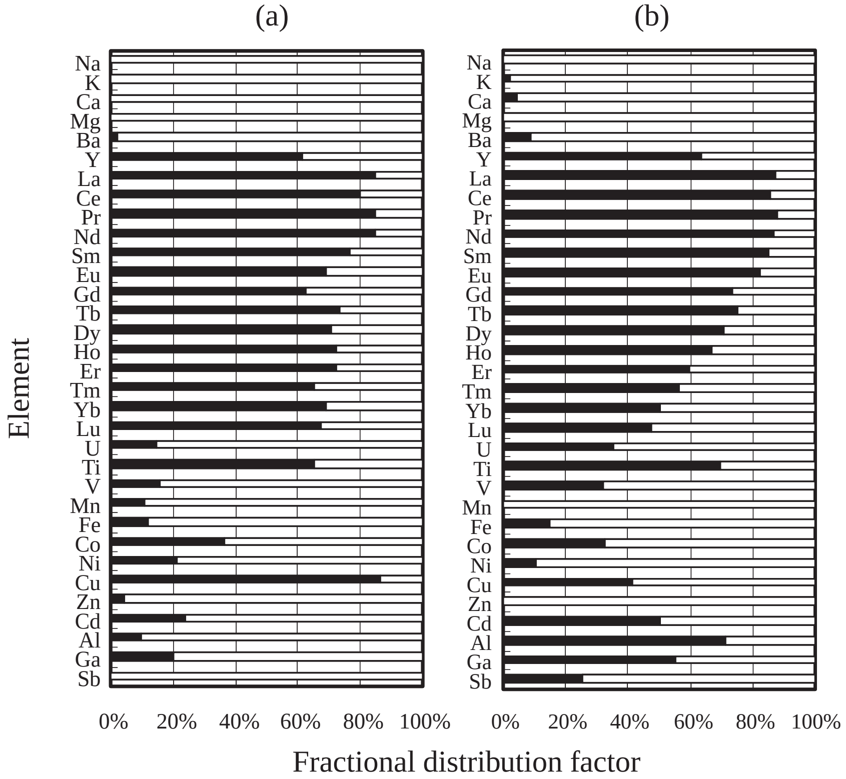

Fig. 1. Fractional distributions of trace metals in LMWFs and SMWFs of surface water from Lake Biwa. (a) Sampling station No. 1 near Hikone. (b) Sampling station No. 2 near Otsu. ▬: LMWF, ▭: SMWF.

enrichment factor (EF) is often employed to examine their relative abundances to the continental crust.[15] The definition of EF is expressed by the following equation,

$$\mathrm{EF} = \frac{[\mathrm{M}]_{\mathrm{sample}}/[\mathrm{Al}]_{\mathrm{sample}}}{[\mathrm{M}]_{\mathrm{crust}}/[\mathrm{Al}]_{\mathrm{crust}}}, \tag{3}$$

where $[\mathrm{M}]_{\mathrm{sample}}$ and $[\mathrm{Al}]_{\mathrm{sample}}$ are the concentrations for the analyte element and Al in the sample, and $[\mathrm{M}]_{\mathrm{crust}}$ and $[\mathrm{Al}]_{\mathrm{crust}}$ are those for the analyte element and Al in the continental crust, respectively. In the above definition, Al was chosen as the normalization element for the calculation of EF, because Al is a hardly-weathered or chemically-inactive element in various geochemical samples. According to the definition of EF, when the EF for a trace metal is close to one, it means that the sample containing the trace metal might have originated from the constituents of the continental crust such as rocks and clays. On the other hand, if a trace metal is relatively enriched in the sample, its EF value is supposed to be larger than one.

The EF values for trace metals in LMWFs were calculated from the data in Tables 3 and 4, and are shown in Fig. 2 in the order of the elemental groups in the periodic table. The data for continental crust were cited from the reference by Taylor and Mclennan.[29] It is seen from Fig. 2 that the EF values for Ti were close to one at both stations, which indicates that Ti mainly originated from the particulates of rocks and clays. Iron and Ga also provided relatively small EF values of less than 10 at station No. 2. These results may also indicate the relatively large contributions of rock and clay particulate in LMWF at station No. 2. In general, however, the EF values for most trace metals in both LMWFs were larger than 10. These facts suggest that various trace metals, especially Cu, Zn, and REEs, are concentrated in LMWF of surface water.

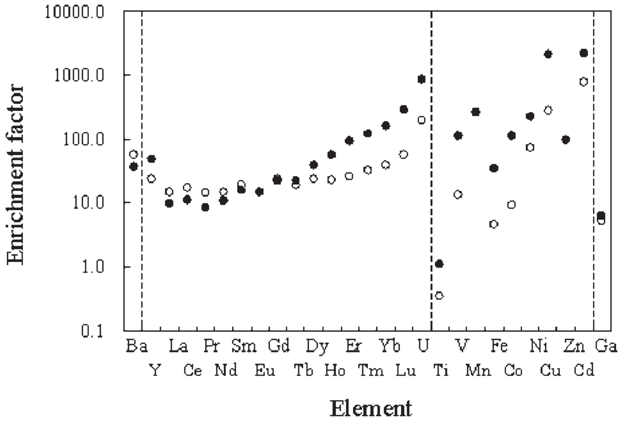

Fig. 2. Enrichment factors for trace metals in LMWFs of surface water from Lake Biwa. ●: Sampling station No. 1 near Hikone. ○: Sampling station No. 2 near Otsu.

The present authors previously reported the formation of colloidal large organic molecule–metal complexes (LOMMCs) in natural waters from Lake Biwa as well as from pond water.[15,30] Such LOMMCs were detected by SEC (size exclusion chromatography)/ICP-AES (and ICP-MS) in a preconcentrated lake or pond water by ultrafiltration. This formation mechanism of colloidal LOMMCs was proposed as the "string-ball model,"[2,15,30] where LOMMCs are formed from fine core particles of minerals coated with colloidal hydroxides

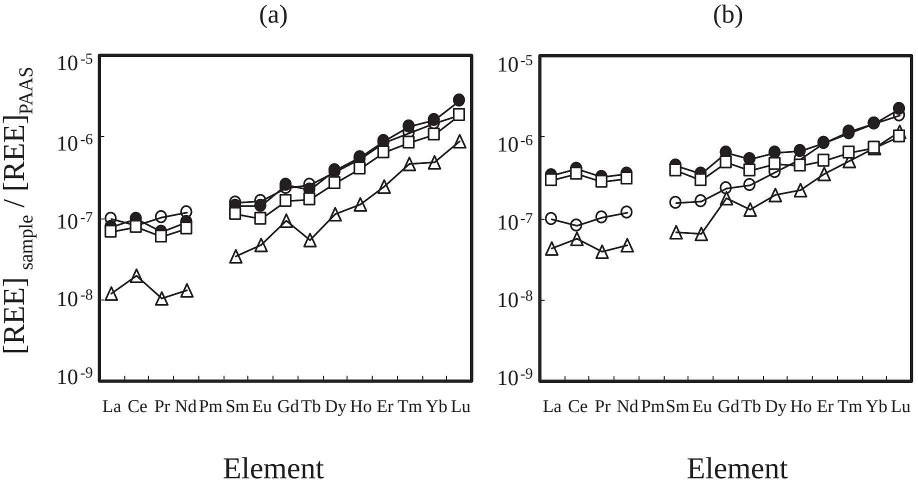

Fig. 3. Shale-normalized REE distribution patterns for the dissolved fractions of surface water from Lake Biwa. (a) Sampling station No. 1 near Hikone. (b) Sampling station No. 2 near Otsu. ●: TDFs, □: LMWF, △: SMWF, and ○: Cited from Ref. 23.

of Al and Fe, biogenic organic molecules, and trace metals. Such colloidal LOMMCs are a kind of particles produced in natural water, and then are called "hydrogenic particles."[2,30] In general, the formation of hydrogenic particles is the main concentration mechanism of most metallic ions in natural water, and the size-growth of hydrogenic particles causes the sedimentation of biogenic organic molecules and metallic ions to produce lake or pond sediment. Thus, the large EF values of various heavy metals in LMWFs shown in Fig. 2 may be explained by the string-ball model, through which trace metals in lake water are concentrated in LMWFs.

Shale-Normalized REE Distribution Patterns for TDF, SMWF, and LMWF Fractions. Shale normalization is commonly used for evaluating the distributions of REEs in natural waters, because shales have typical REE contents of sedimentary rocks.[27–29] The shale-normalized REE distribution patterns for the fractions (TDF, LMWF, and SMWF) obtained from the data in Tables 3 and 4 are shown in Figs. 3a and 3b, where the concentrations of REEs in each fraction were normalized to those in post-Archean average Australian shale (PAAS)[29] and plotted against atomic number. Consequently, the Y-axis in Figs. 3a and 3b is shown as $[REE]_{sample}/[REE]_{PAAS}$, where $[REE]_{sample}$ and $[REE]_{PAAS}$ indicate the concentrations of REEs in the sample and those in PAAS, respectively. It is seen in Fig. 3 that the REE distribution patterns for TDFs, SMWFs, and LMWFs from both stations showed typical dissolved REE contents in natural waters, i.e., the relatively lower concentrations for light REEs and the relatively higher concentrations for heavy REEs. However, it should be noted here that the REE distribution patterns of LMWF in Fig. 3 showed much higher abundances than those of SMWF. These results indicate that REEs were concentrated much higher in LMWF than in SMWF, which suggests that LMWFs were composed of some hydrogenic particulates produced through the string-ball model, as explained above.[15] In addition, it is also noticed that the REE distribution patterns in Fig. 3a showed much higher relative abundances of heavy REEs than those of light REEs. This may indicate that surface water from station No. 1 contained more organic matter, because heavy REEs generally have chemical properties to form complexes with organics more than light REEs.[27] On the other hand, it is seen in Fig. 3 that the REE distribution patterns in the station No. 2 were different from those in station No. 1. In the latter case, the relatively higher concentrations of light REE contents were observed. The relatively large concentrations of light REEs in LMWF and TDFs in station No. 2 may indicate that fine mineral particulates forming core materials of colloidal LOMMCs might be contained more in surface water at station No. 2 than at station No. 1, as discussed in the section of the fractional distribution factor.

The REE pattern for the concentrations of REEs in surface water from Lake Biwa reported by Haraguchi et al.[23] is also plotted in Fig. 3, where the samples were filtered with a membrane filter (pore size 0.45 µm), and thus their concentrations are corresponding to those in TDFs in the present experiment. The samples examined by Haraguchi et al. were collected in November, 1993, while the present ones were collected in December, 2002. It is seen in Fig. 3 that the concentrations of REEs in TDFs at station No. 1 were almost coincident with the reported ones, while the concentrations of light REEs in TDFs at station No. 2 were significantly higher than those in the reported ones, although the concentrations of heavy REEs in TDF were coincident with each other. These results also suggest the contributions of terrestrial mineral particulates to the concentrations of REEs in surface water at station No. 2, as described above.

Furthermore, it should be noted here that the results for all fractions examined in the present experiment showed some positive anomalies of Ce and Gd in the shale-normalized REE distribution patterns; the concentrations of Ce and Gd, especially in SMWFs, were relatively higher than those of their neighboring REEs. In general, natural waters such as river water, lake water, and seawater show a negative anomaly of Ce,[31,32] because Ce^{3+} is readily oxidized to Ce^{4+} in natural water and precipitates as CeO_2, while other REEs except for Eu remain in the 3+ oxidation state and do not cause their fractionations.[27] The apparent positive anomaly of Ce in Lake Biwa suggests the occurrence of some environmental change due to anthropogenic discharge in the last decade. One of the possible sources of Ce discharge may be automobile exhaust particles, as suggested by Silva and Prather.[33] According to Silva and Prather's research,[33] in recent years, the increase in Ce contained in the exhaust of recent automobiles is due to the increased use for exhaust gas catalysts, instead of the disappearance of lead contents due to the use of unleaded gasoline.

On the other hand, in recent years, a positive anomaly of Gd has been reported for river waters and coastal seawaters around Tokyo and Nagoya in Japan[34,35] as well as for those around the urban areas of Germany[36,37] and France.[38] All those reports conclusively pointed out that the increase of Gd causing its positive anomaly is attributed to the wide use of $[Gd(dtpa)]^{2-}$ (diethylenetriaminepentaacetato gadolinite(III)) as a contrast reagent for MRI (magnetic resonance imaging) diagnosis in hospitals. From the experimental results obtained in Fig. 3, thus, a positive anomaly of Gd in surface water from Lake Biwa, especially in SMWF, also suggests that the increase in the Gd concentration has been progressing artificially as the result of anthropogenic emission of $[Gd(dtpa)]^{2-}$ around Lake Biwa.

Conclusion

The fractional distributions of trace metals in surface water from two sampling stations of Lake Biwa were investigated by the determination of various trace metals in the fractionated samples, i.e., TDFs, SMWFs, and LMWFs. Based on the concentrations of trace metals, their enrichment factors and REE distribution patterns, it was found that LMWFs were composed of hydrogenic particulates containing soluble organic complexes and trace metals as colloidal LOMMCs. Furthermore, positive anomalies of Ce and Gd caused by anthropogenic emission were also found in all fractions investigated in the present experiment. In conclusion, it is strongly recommended that further investigation on the emission sources of these elements is required including in Lake Biwa.

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