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RESEARCH PAPER

Lake Biwa and the ocean: geochemical similarity and difference

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Abstract The average composition of water, bottom sediments, manganese (Mn) crusts, and Mn concretions from Lake Biwa (the largest freshwater lake in Japan) are re-examined, in conjunction with those of seawater, oceanic pelagic clay, and deep-sea Mn nodules. The purpose is to gain additional insights into the geochemical behaviors of elements in Lake Biwa and the ocean, which are quite different in ionic strength (or salinity), pH, water residence times, sediment accumulation rates, carbon fluxes to sediments, and the redox potential in sediments. Excluding a few millimeters of oxic surface sediment, there is no appreciable accumulation of Mn in the Lake Biwa bottom sediments due to reducing condition there. Consequently, other B-type cations [such as iron (Fe), gallium (Ga), copper (Cu), lead (Pb), cobalt (Co), tin (Sn), and bismuth (Bi), with subshell valence electron configuration of d^{1-10}] are also less concentrated in the lake sediments than in the oceanic pelagic clay. In turn, B-type cations have much higher dissolved concentrations in the lake water than in the ocean. The rare earth elements (REE) mainly form organic complexes in the lake water and carbonate complexes in the ocean. REE are mostly associated with detritus aluminosilicate phases in Lake Biwa sediments but with phosphate phases in deep-sea sediments. Fe and Mn oxide phases are clearly separated in marine Mn nodules and crusts but not in Mn crusts and concretions from Lake Biwa. Useful parameters such as the enrichment factor (E_{Al}) and logarithms of the distribution coefficient (log K_d) of elements between solid and liquid phases were estimated in both systems for further discussions.

Keywords Lake Biwa · Ocean · Chemical compositions · Enrichment factor · Distribution coefficient

Abbreviations: See table footnotes for element abbreviations

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Introduction

Lake Biwa, located east of Kyoto, is the largest freshwater lake in Japan (Fig. 1) and was formed about 5 million years ago (Horie 1984). Many scientific studies on Lake Biwa were summarized in Horie (1984), Takamatsu (1985), Fujinaga et al. (2005, and references therein), and Li et al. (2007). Hydrological parameters of Lake Biwa are significantly different from those of the ocean. Mass balances of water in Lake Biwa and the ocean are listed in Table 1. The residence time of water in the southern (S-) basin is only 14 days compared with 5.3 years in the northern (N-) basin. Since the S-basin is much smaller than the N-basin, the term Lake Biwa hereafter in this paper indicates the N-basin. For comparison, the residence time of water in the surface (average depth of 100 m) and deep (average depth of 3,700 m) oceans are, respectively, about 24 and 1230 years, assuming the water exchange rate between the surface and deep oceans is about 3 m^3/m^2 year (Broecker and Peng 1982) and the world river runoff is 37×10^{12} m^3/year (Berner and Berner 1987). The mean pH of Lake Biwa water is about 7.3 during winter mixing

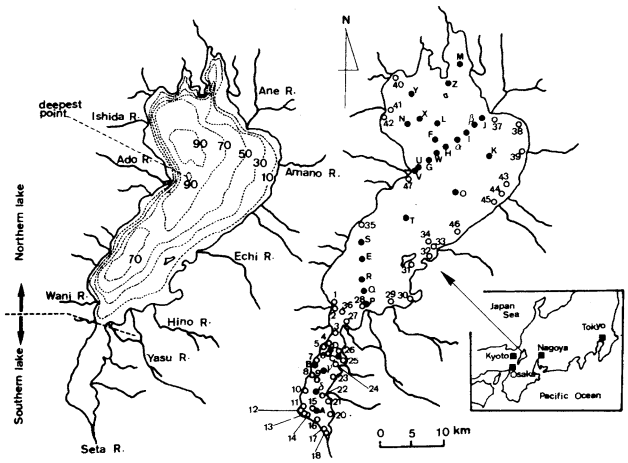

Fig. 1 Bathymetry and sampling locations for dredged (*numbers*) and core (*alphabets*) sediments in Lake Biwa (adopted from Takamatsu 1985)

(Mito et al. 2004), whereas the deep-ocean pH is about 7.6 (Broecker and Peng 1982).

The average accumulation rates of clay sediments in Lake Biwa and the ocean are, respectively, about 80 mg/cm^2 (Yamamoto 1984) and 0.3 mg/cm^2 (Ku et al. 1968) year, or about 500 and 2 mm/10^3 year (assuming density of 1.5 g/cm^3). The average organic carbon contents of Lake Biwa surface sediments at water depth below 20 m and oceanic pelagic clays are, respectively, about 3% and 0.45% (Murase and Sakamoto 2000; Li 2000); thus, the organic carbon flux to sediments are, respectively, about 2,400 and 1.4 μg C/cm^2/year. As mentioned by Dr. Michio Kumagai at the Lake Biwa Environmental Research Institute (personal communication), nitrate concentration in Lake Biwa water samples taken yearly 1 m above the bottom sediments at a water depth of 80 m has increased more or less linearly from 50 to 260 μg N/l between 1950 and 2000. Concurrently, the lowest concentration of dissolved oxygen in the same samples taken during summer season has decreased from about 8 down to 4 mg O_2/l. The implication is that the organic carbon flux from the surface lake to deep water and sediments also have increased during the same period due to gradual eutrophication of the lake. The dissolved oxygen concentration of the ocean bottom water is about 8.3 mg O_2/l in the northern Atlantic, decreases to about 7.0 mg O_2/l in the Antarctic, and to about 4.8 mg O_2/l in the northern Pacific (Broecker and Peng 1982; also see http://ewoce.org/gallery). As shown by Jahnke et al. (1989), pelagic sediment cores taken from the equatorial Atlantic are highly oxic [as inferred from high nitrate, low dissolved Mn concentrations, and detectable O_2 in pore waters], even down to 20–40 cm below the water–sediment interface. In contrast, the pore water becomes anoxic just 0.2–0.3 cm below the water–sediment interface

Table 1 Mass balance of water in Lake Biwa and the ocean

	Lake Biwa			Ocean
	Total	N-basin	S-basin	
Surface area (km^2)	674	616	58	360 × 10^6
Volume (km^3)	27.3	27.1	0.2	1370 × 10^6
Mean depth (m)	41	44	3.5	3800
Precipitation (km^3/years)	1.2			386 × 10^3
Evaporation (km^3/years)	0.6			423 × 10^3
River inflow (km^3/years)	2.8			37 × 10^3[a]
Groundwater inflow (km^3/years)	1.2			
River outflow (km^3/years)	4.6	~4.6	4.6	
Residence time of water τ_w (years)	5.3[b]	5.3	0.043	24 (surface)
				1230 (deep)

Data sources: precipitation, evaporation, and river outflow data are from Kotoda and Mizuyama (1984); river inflow from Somiya (2000); and groundwater inflow by water mass balance; Lake Biwa areas, volumes, and mean depths are from the Lake Biwa Research Institute (1988). Data for the ocean are from Berner and Berner (1987)

[a] Including groundwater contribution

[b] The mean residence time of water (τ_w) in the lake is calculated as the lake volume divided by the river outflow rate plus water evaporation rate over the lake

in the deep Lake Biwa due to high organic matter flux and its rapid oxidation by bacteria in sediments (Takamatsu et al. 1985b; Fujinaga et al. 2005).The accumulation rate of Mn concretions in Lake Biwa is not yet determined, but Mn concretions in Oneida Lake (in central New York State) accrete at a rate of more than 2 mm/year (Dean et al. 1973), which is six orders of magnitude faster than that for the ocean Mn nodule (a few mm/million years; Ku and Broecker 1967). Because the composition of water, bottom sediments, Mn concretion, and Mn crust have been studied extensively both in Lake Biwa and the ocean, it is worthwhile to re-examine some of those data in order to gain new insights into the geochemical behavior of elements in these two contrasting aquatic systems.

Materials and methods

The average concentrations of dissolved elements in Lake Biwa water (C_{LB}; Sugiyama 2005; Haraguchi et al. 1998; Zhu et al. 2005) and in seawater [C_{SW}; Li 2000, and newer data from Orians and Merrin 2001, for Bi, Fe, In, Th, and Ti; Ravizza 2001, for Ir, Os, Pt, Rh; and Firdaus et al. 2008, for Hf, Mo, Nb, Ta, and W) are summarized in Table 2. The dissolved elements are usually defined as the elements passing through a 0.45-μm pore-size filter. The chemical data for sediments (see Fig. 1 for sample locations), Mn

Table 2 Atomic number (Z); average compositions of Lake Biwa water (C_{LB}), and the seawater (C_{SW}) in units of 10^{-9} g/l

Ele.	Z	Lake Biwa C_{LB} (1)	Seawater C_{SW} (2)	Ele.	Z	Lake Biwa C_{LB} (1)	Seawater C_{SW} (2)
Ag	47	3.1	2.5	Mo	42	280	10E+3
Al	13	540	300	N	7	20E+4	42E+4
As	33	970	1700	Na	11	67E+5	108E+8
Au	79		0.03	Nb	41		0.67 f
B	5	13E+3	45E+5	Nd	60	3.7 h	4.2
Ba	56	8E+3	15E+3	Ni	28	205	530
Be	4	0.41	0.21	Os	76		0.01 r
Bi	83	0.16	0.029 o	P	15	5.6E+3	65E+3
Br	35	13E+3	67E+6	Pb	82	54	2.7
C	6		28E+6	Pd	46		0.07
Ca	20	11E+6	450E+6	Pr	59	0.91 h	0.87
Cd	48	3.0	76	Pt	78		0.05 r
Ce	58	6.5 h	1.6	Rb	37	1450	12E+4
Cl	17	74E+5	188E+8	Re	75		8
Co	27	11.8	1.2	Rh	45		0.1 r
Cr	24	42.6	250	Ru	44		0.002 r
Cs	55	5.9	310	S	16	2.9E+6	898E+6
Cu	29	500	210	Sb	51	180	150
Dy	66	1.6 h	1.5	Sc	21	0.16	0.86
Er	68	2.3 h	1.3	Se	34	40.3	145
Eu	63	0.18 h	0.21	Si	14	5.3E+5	25E+5
F	9	13E+4	130E+4	Sm	62	0.9 h	0.84
Fe	26	1340	30 o	Sn	50	8.7	0.6
Ga	31	4.7 z	1.2 o	Sr	38	4.2E+4	780E+4
Gd	64	1.1 h	1.3	Ta	73	0.02	0.04 f
Ge	32		4.3	Tb	65	0.20 h	0.21
Hf	72	0.04	0.13 o	Te	52		0.07
Hg	80		0.42	Th	90	0.03	0.02 o
Ho	67	0.53 h	0.45	Ti	22	6.2	6.7 o
I	53		58E+3	Tl	81		14
In	49		0.011 o	Tm	69	0.45 h	0.25
Ir	77		0.0001 r	U	92	17	3200
K	19	1.8E+6	390E+6	V	23	120	2150
La	57	4 h	5.6	W	74	6.6	9 f
Li	3	400	180E+3	Y	39	12	13
Lu	71	0.79 h	0.32	Yb	70	4.1 h	1.5
Mg	12	21E+5	13E+8	Zn	30	150 s	320
Mn	25	1370	72	Zr	40		16 o

Data sources: *(1)* Sugiyama (2005); *(2)* Li (2000, and references therein); *f* Firdaus et al. (2008); *h* Haraguchi et al. (1998); *o* Orians and Merrin (2001); *r* Ravizza (2001); *s* Sugiyama et al. (2005); *z* Zhu et al. (2005)

Ag silver, *Al* aluminum, *As* arsenic, *Au* gold, *B* boron, *Ba* barium, *Be* beryllium, *Bi* bismuth, *Br* bromine, *C* carbon, *Ca* calcium, *Cd* cadmium, *Ce* cerium, *Cl* chlorine, *Co* cobalt, *Cr* chromium, *Cs* cesium, *Cu* copper, *Dy* dysprosium, *Er* erbium, *Eu* europium, *F* fluorine, *Fe* iron, *Ga* gallium, *Gd* gadolinium, *Ge* germanium, *Hf* hafnium, *Hg* mercury, *Ho* holmium, *I* iodine, *In* indium, *Ir* iridium, *K* potassium, *La* lanthanum, *Li* lithium, *Lu* lutetium, *Mg* magnesium, *Mn* manganese, *Mo* molybdenum, *N* nitrogen, *Na* sodium, *Nb* niobium, *Nd* neodymium, *Ni* nickel, *Os* osmium, *P* phosphorus, *Pb* lead, *Pd* palladium, *Pr* praseodymium, *Pt* platinum, *Rb* rubidium, *Re* rhenium, *Rh* rhodium, *Ru* ruthenium, *S* sulfur, *Sb* antimony, *Sc* scandium, *Se* selenium, *Si* silicon, *Sm* samarium, *Sn* tin, *Sr* strontium, *Ta* tantalum, *Tb* terbium, *Te* tellurium, *Th* thorium, *Ti* titanium, *Tl* thallium, *Tm* thulium, *U* uranium, *V* vanadium, *W* tungsten, *Y* yttrium, *Yb* ytterbium, *Zn* zinc, *Zr* zirconium

concretion (Takamatsu et al. 1985a), and Mn crust (Takamatsu et al. 1993) from Lake Biwa are summarized in Table 3, along with some additional sediment data from Teraoka and Kobayashi (1980) for Be, Koyama et al. (1984) for Al and Si, and Haraguchi et al. (1998) for rare earth elements (REE). The corresponding data for the ocean in Table 3 are from Li (2000, and references therein), except for REE, which are adopted from Takebe (2005). For the world's average shale composition (Table 3), the original Br = 20 ppm and Ni = 50 ppm given by Li (2000) are too high for the Lake Biwa region and are replaced by the average soil values of Br = 5 ppm and Ni = 30 ppm (Li 2000).

We applied the concept of enrichment factor (E_j^i) to highlight the difference and similarity between a given sample and a chosen reference material. Here the enrichment factor is defined as the concentration ratio of element i and the normalizing element $j(X_i/X_j)$ in a given sample divided by the same ratio in a chosen reference material, i.e.,

$$E_j^i = \frac{(X_i/X_j)_{\text{sample}}}{(X_i/X_j)_{\text{reference}}}$$

For example, when a sample is normalized to Al and compared with shale, one may write E_{Al}^i(sample/shale), or just E_{Al}(shale). $E_j^i > 1$ means the sample is enriched in element i relative to the reference material, and $E_j^i < 1$ means depleted. If one wishes to normalize to a third element k, then, E_k^i is simply equal to E_j^i/E_j^k. When $E_j^k \approx 1$, then $E_k^i \approx E_j^i$.

When ion i in solution and solid phase are in chemical equilibrium, one may write the overall reaction schematically:

$$C_i \leftrightarrow X_i \tag{1}$$

Here C_i is the concentration of dissolved ion i in the solution (in units of mass per cm^3 of solution) and X_i in the solid phase (in units of mass per gram of solid phase). At equilibrium, the following equations hold:

$$K_{\text{d}} = \frac{X_i}{C_i}(\text{cm}^3/\text{g}) = \frac{\gamma_i(\text{solution})}{\gamma_i(\text{solid})} \exp\left(\frac{-\Delta G_{\text{r}}}{\text{RT}}\right) \tag{2a}$$

or

$$\log K_{\text{d}}^i = \log\frac{X_i}{C_i} = \log\frac{\gamma_i(\text{solution})}{\gamma_i(\text{solid})} + \frac{-\Delta G_{\text{r}}}{2.3\text{RT}} \tag{2b}$$

Here K_{d}^i is the apparent equilibrium constant and is also called the distribution or partition coefficient of ion i between solid and solution; and ΔG_{r} is the Gibbs free energy of reaction 1. Log K_{d}^i is directly proportional to $-\Delta G_{\text{r}}$ at constant temperature as long as the activity coefficient ratio γ_i(solution)/γ_i(solid) does not change much from ion to ion (it is the case for ions with very

Table 3 Average compositions of shale (X_{sh}); oceanic pelagic clay (X_{op}) and manganese nodules (X_{mn}); Lake Biwa sediments 10 cm below core top (X_{10}) and top 2 cm (X_2); top part of Lake Biwa Mn-crust (X_t) and bottom part (X_b); and Lake Biwa Mn-concretion (X_c)

Ele.	Shale	Ocean clay	Biwa sediments		Ocean nodules	Biwa Mn crust		Biwa
			>10 cm	<2 cm		Top	Bottom	Mn-con.
	X_{sh} (1)	X_{op} (1)	X_{10} (2)	X_2 (2)	X_{mn} (1)	X_t (3)	X_b (3)	X_c (2)
Ag	0.07	0.11			0.09			
Al (%)	8.8	8.4	11.4 k	10.5 k	2.7	4.1	2.4	4.9
As	13	20	23	55	140	700	1280	721
Au (ppb)	2.5	2			2			
B	100	230			300	200	330	
Ba	580	2300	680	690	2300	560	3820	1389
Be	3	2.6	3 te	3 te	2.5	2.7	7.1	
Bi	0.43	0.53			7			
Br	5 li		7	9	21	1.4	2.2	14.3
Ca (%)	1.6	1	0.34	0.37	2.3	0.36	0.85	0.43
Cd	0.3	0.42			10			
Ce	82	89.7 t	85 h	78 h	530	29	41	39.6
Co	19	74	17.8	17.6	2700	22	87	23.8
Cr	90	90	70	67	35	16	22	37.2
Cs	5	6	10.8	10.4	1	2.2	8.3	5.0
Cu	45	250	52	76	4500	24	99	60
Dy	4.7	8.19 t	5.8 h	5.3 h	31			
Er	3	4.79 t	3.6 h	3.3 h	18			
Eu	1.2	2.03 t	1.1 h	1.0 h	9	0.4	0.9	
F	740	1300			200			
Fe (%)	4.72	6.5	4.57	4.53	12.5	20.8	32.5	3.1
Ga	19	20			10			
Ge	1.6	1.6			0.8			
Gd	5.1	8.73 t	6.8 h	6.3 h	32			
Hf	5	4.1	5.2	4.8	8	2.4	0.8	1.9
Hg	0.18	0.1	0.12	0.19	0.15			
Ho	1.1	1.67 t	1.2h	1.1 h	7			
I	19	28			400			
In	0.1	0.08			0.25			
Ir (ppb)	0.05	0.4			7			
K (%)	2.66	2.5	2.49	2.4	0.7	2.23	0.72	1.32
La	43	40.2 t	44 h	40 h	157	12.7	26.8	21.5
Li	66	57			80			
Lu	0.42	0.64 t	0.54 h	0.5 h	1.8	0.25	0.36	0.27
Mg (%)	1.5	2.1	0.96	0.97	1.6	0.12	0.12	1.01
Mn (%)	0.085	0.67	0.186	0.376	18.6	0.75	5.51	16.7
Mo	2.6	27			400			
N	1000	600	1900	3020	200			
Na (%)	0.59	2.8	0.86	0.93	1.7	0.68	0.23	0.86
Nb	11	14			50			
Nd	33	42 t	36.5 h	33.6 h	158			28
Ni	30 li	230	30	33	6600	16	105	340
Os (ppb)	0.05	0.14			2			
P (%)	0.07	0.15	0.083	0.115	0.25	0.68	1.14	0.27
Pb	20	80	32	51	900	17	15	26
Pd (ppb)	1	6			6			

Table 3 continued

Ele.	Shale	Ocean clay	Biwa sediments		Ocean nodules	Biwa Mn crust		Biwa
			>10 cm	<2 cm		Top	Bottom	Mn-con.
	X_{sh} (1)	X_{op} (1)	X_{10} (2)	X_2 (2)	X_{mn} (1)	X_t (3)	X_b (3)	X_c (2)
Pr	9.8	10.1 t	9.0 h	8.3 h	36			
Pt (ppb)	1	5			200			
Rb	140	110	139	131	17	96	31	70
Re (ppb)	0.4	0.3			1			
Rh (ppb)		0.4			13			
Ru (ppb)		0.2			8			
S	2400	2000			4700			
Sb	1.5	1	1.9	3.2	40	3	9.1	5.5
Sc	13	19	14.5	13.4	10	3.1	1.9	7.5
Se	0.6	0.2			0.6			
Si (%)	27.5	25	26.6 k	23.9 k	7.7	19	9.3	27.3
Sm	6.2	8.69 t	8.2 h	7.5 h	35	2.5	5	4.6
Sn	3	4			2			
Sr	170	180	76	72	830	35	99	103
Ta	1	1	1.2	1.1	10			0.8
Tb	0.84	1.32 t	1.04 h	0.96 h	5.4	0.4	0.8	
Te	0.07	1			10			
Th	12	13	16.6	15.5	30	5.8	2.4	9.2
Ti	4600	4600	5000	4500	6700	800	500	2900
Tl	0.7	1.8			150			
Tm	0.44	0.67 t	0.53 h	0.49 h	2.3			
U	2.7	2.6	3.4	3.5	5	2.3	3	4.9
V	130	120			500	110	265	
W	1.8	4			100			
Y	26	40			150			
Yb	2.8	4.23 t	3.7 h	3.4 h	20	1.5	2.1	2.0
Zn	95	170	135	203	1200	73	215	189
Zr	160	150			560			

All are in units of ppm unless noted otherwise. X_{mn} values for Nb and Ta are less reliable

Data sources: *(1)* Li (2000), *(2)* Takamatsu (1985) and Takamatsu et al. (1985b), *(3)* Takamatsu et al. (1993); *h* Haraguchi et al. (1998); *k* Koyama et al. (1984), assuming Al/Sc and Si/Sc ratios are constant; *li* average soil in Table VI-5a of Li (2000); *t* Takebe's (2005) sample NB50, which has P_2O_5 content similar to that of the average ocean pelagic clay; *te* Teraoka and Kobayashi (1980)

Ag silver, *Al* aluminum, *As* arsenic, *Au* gold, *B* boron, *Ba* barium, *Be* beryllium, *Bi* bismuth, *Br* bromine, *Ca* calcium, *Cd* cadmium, *Ce* cerium, *Co* cobalt, *Cr* chromium, *Cs* cesium, *Cu* copper, *Dy* dysprosium, *Er* erbium, *Eu* europium, *F* fluorine, *Fe* iron, *Ga* gallium, *Gd* gadolinium, *Ge* germanium, *Hf* hafnium, *Hg* mercury, *Ho* holmium, *I* iodine, *In* indium, *Ir* iridium, *K* potassium, *La* lanthanum, *Li* lithium, *Lu* lutetium, *Mg* magnesium, *Mn* manganese, *Mo* molybdenum, *N* nitrogen, *Na* sodium, *Nb* niobium, *Nd* neodymium, *Ni* nickel, *Os* osmium, *P* phosphorus, *Pb* lead, *Pd* palladium, *Pr* praseodymium, *Pt* platinum, *Rb* rubidium, *Re* rhenium, *Rh* rhodium, *Ru* ruthenium, *S* sulfur, *Sb* antimony, *Sc* scandium, *Se* selenium, *Si* silicon, *Sm* samarium, *Sn* tin, *Sr* strontium, *Ta* tantalum, *Tb* terbium, *Te* tellurium, *Th* thorium, *Ti* titanium, *Tl* thallium, *Tm* thulium, *U* uranium, *V* vanadium, *W* tungsten, *Y* yttrium, *Yb* ytterbium, *Zn* zinc, *Zr* zirconium

low concentration in solution) or the log γ_i(solution)/γ_i(solid) term is always much smaller than the absolute value of $\Delta G_r/(2.3RT)$ for most elements. A high log K_d^i value (i.e., high log X_i/C_i, or negative ΔG_r) indicates the high tendency for ion i to concentrate in solid phase rather than in solution (i.e., high reactivity to particles), and vice versa.

The K_d^i is related to the mean residence time of element i in a water column (τ^*_i) with regard to its removal to bottom sediments. All other possible removal pathways (such as output through water–air interface, outflow flux from a lake, removal at hydrothermal vents etc.) are not included here. The definition of τ^*_i, as proposed by Goldberg and Arrhenius (1958), is:

$$\tau_i^*(\text{years}) = V \cdot C_i/(F \cdot X_i) \propto C_i/X_i \quad (3a)$$

or

$$1/\tau_i^* \propto X_i/C_i = K_d^i \quad (3b)$$

where V, volume of water body; C_i, average concentration of dissolved element i in the water body; F, total sediment flux to the bottom of water body; and X_i, average concentration of element i in the bottom sediments. Both V and F are considered as near constants here. A large log τ^* value reflects low reactivity to particles, and vice versa.

Li (1982, 2000, 2008) demonstrated that the log K_d in the ocean (=log X_{op}/C_{SW}) is positively correlated with I_z (electron binding energy to gaseous ion with charge z for the forward reaction M^{+z} (g) + $e^- \rightarrow M^{z-1}$(g) + I_z; for the reverse reaction, I_z is also called ionization potential or energy) for cations with charge 1–4, and negatively correlated with I_z for metals that have charge of 4 or greater and exist as hydroxyl complexes and oxyanions in the ocean. This up-and-down relationship between log X/C and I_z is named the "Λ" (Greek capital letter lambda) relationship (Li 2008). As shown by Li (1982, 2008), this "Λ" relationship can be explained by the surface complexation model of cations and anions onto hydrolyzed surface of oxide particles (Stumm et al. 1970; Schindler 1975; Stumm and Morgan 1981).

Since the average concentrations of many dissolved elements are well known in water, sediments, and Mn crusts of Lake Biwa (Table 3), the concepts of distribution coefficient and the surface complexation model can be fruitfully applied to the Lake Biwa system. It will elucidate the importance of chemical equilibrium between liquid and solid phases and the relative reactivity of elements to suspended particles and sediments in the lake compared with those in the ocean (Li 2000).

Results and discussion

Average composition of Lake Biwa water

In the plot of the concentrations of dissolved elements in Lake Biwa (C_{LB}) versus those in seawater (C_{SW}) (Fig. 2), the elements are separated into s-, p-, d-, and f-blocks according to which subshell is filled in by the last valence electron. The asterisk symbols without label in Fig. 2 are REE. Each block is subdivided further into A-type ions that have electron configurations of noble gases or contain f-subshell valence electrons, and B-type ions that contain d-subshell valence electrons. The d-subshell electrons in B-type ions tend to be easily polarized under the influence of external electric field and tend to form strong chemical bonding, especially for fully filled d^{10} cations (Stumm and Morgan 1981; Li 2000). The solid line in Fig. 2 represents the concordant line (log y = log x), and two dotted lines are deviated from the concordant line by a factor of two (log y = log $2x$ and log y = log $x/2$).

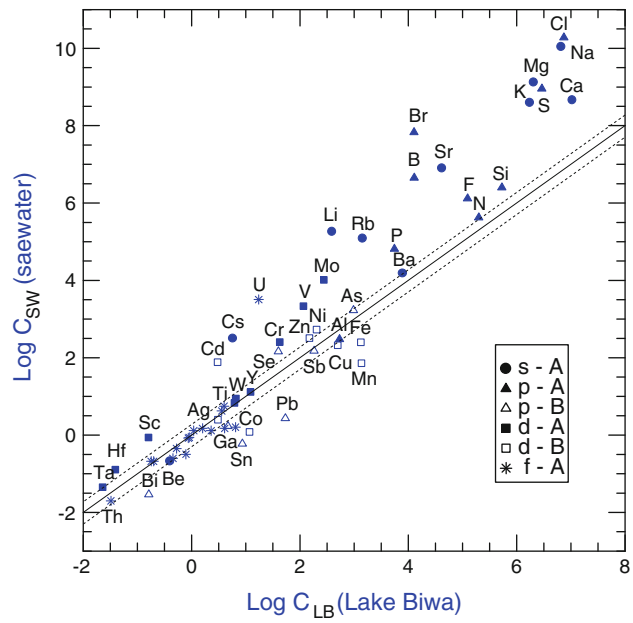

Fig. 2 The average concentrations of elements (10^{-9} g/l) in Lake Biwa water (C_{LB}) versus that in seawater (C_{SW}). All in logarithm scale. Elements are classified into s-, p-, d-, and f-blocks, and A- and B-types (see text)

A-type ions with dissolved concentration greater than that of Cr in seawater (such as cations of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba; anions of F, Cl, Br; and oxyanions of N, P, Si, B, Mo, V, and Cr) tend to have much higher concentrations in seawater than in Lake Biwa (Fig. 2). Those same elements also have relatively long mean residence times (>10^4 years) and less particle reactivity in the ocean (Li 2000). One exception is Ba, the mean residence time of which is <10^4 years, indicating additional removal mechanisms of Ba in the ocean, such as formation of biogenic barite ($BaSO_4$; Dehairs et al. 1980; Bertram and Cowen 1997). For ions with dissolved concentration less than that of Cr in seawater, A-type cations (Y, REE, Ti, Sc, Be, Hf, Th, and Ta) tend to have similar concentrations in the lake and the ocean; and B-type ions (Fe, Mn, Ga, Cu, Pb, Co, Sn, and Bi) tend to have higher concentrations in Lake Biwa than in seawater. One obvious exception is Cd, which is relatively high in seawater. One possible explanation is that Cd^{2+} forms the strongest chloride complex among all divalent cations in seawater (Li 2000). The relative depletion of B-type ions in seawater can be explained by the fact that ubiquitous Mn oxide coating on the oceanic pelagic clay enhances the removal of those elements from the ocean to sediments (Li 2000; Li and Schoonmaker 2004). Except for a few millimeters of oxic surface sediments, the formation of

Mn oxide coating on the anoxic subsurface sediments of Lake Biwa is apparently near nil.

Concentrations of dissolved REE in Lake Biwa water and seawater are normalized by the world's average shale concentrations (X_{sh} in Table 3) and are plotted in Fig. 3 as log C_{LB}/X_{sh} and log C_{SW}/X_{sh} versus atomic number (Z). Interestingly, the shale-normalized REE concentrations are very similar between the lake water and seawater. The obvious exception is Ce, which is much depleted in seawater due to oxidative uptake of Ce ($Ce^{3+} \rightarrow Ce^{4+}$) by marine sediments, Mn nodules, and crusts (Li 1991 and references therein). For REE heavier than Eu, the log C_{LB}/X_{sh} and log C_{SW}/X_{sh} values tend to increase with atomic number, especially in Lake Biwa (Fig. 3). In seawater, the complex formation constants of REE with carbonate ion also increase with their atomic number; thus, the heavier REE become more stable in seawater as carbonate complexes (Erel and Morgan 1991). In a freshwater system like Lake Biwa, REE–carbonate complexes are minor due to relatively low carbonate ion concentration (Stumm and Morgan 1981), but REE form strong complexes with large (10 nm < size < 0.45 μm) and small (<10 nm) molecular weight organic colloids in the Lake Biwa water column (Haraguchi et al. 1998; Zhu et al. 2005). As shown by Aoki et al. (2004), the average concentration of dissolved organic carbon (DOC) in Lake Biwa is 170 ± 30 nM, and humic substances (<5 nm in size) account for 23 ± 9% of DOC. In contrast, DOC in the deep ocean are around 45 ± 5 nM, and most (~75%) are low molecule weight organic carbon (<1 nm; Benner et al. 1997). How important the complex formation of REE with DOC is relative to carbonate ion in the ocean is still an unanswered question.

Average compositions of Lake Biwa sediments

According to the enrichment factor E_{Al}(shale) in Fig. 4a, the average compositions of the Lake Biwa sediments 10 cm below the core top (X_{10}) and the world's average shale (X_{sh}) are essentially the same within a factor of 1 ± 0.3 (within two horizontal dotted lines), including REE ($X_{10} = X_2$ in Fig. 4a). The obvious exceptions are Mg, Ca, and Sr, which tend to be low in Lake Biwa sediments and in suspended particles of rivers flowing into Lake Biwa (Teraoka and Kobayashi 1980), reflecting the preferential leaching of alkaline-earth elements from the outcropping rocks and soils during the weathering process (Li 2000). Also, Mn and Cs are slightly higher in Lake Biwa sediments (X_{10}) than in the average shale (E_{Al}(shale) > 1.5), probably reflecting regional variability.

The top 2 cm of Lake Biwa sediments (X_2) are high in N, P, Mn, Cu, Zn, As, Br, Sb, Hg, and Pb compared with those of X_{10} (Fig. 4a, b). As shown by the factor analysis of sediment data (Li et al. 2007), those enriched elements are mainly associated with both organic matter and hydrous Mn oxide phases in surface sediments. In contrast, the oceanic pelagic clay (X_{op}) is enriched in Na, Mg, P, Ca, Mn, Co, Ni, Cu, Sr, Ba, REE, and Pb relative to those of X_{10} and X_2 (Fig. 4b) but not in As, Sb, and Hg. According

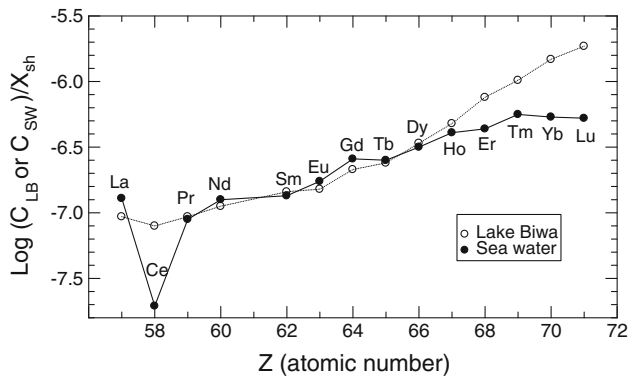

Fig. 3 Shale-normalized rare earth elements (REE) in Lake Biwa (log C_{LB}/X_{sh}) and ocean (log C_{SW}/X_{sh}) waters as a function of atomic number of REE. C/X's are in units of g/cm^3

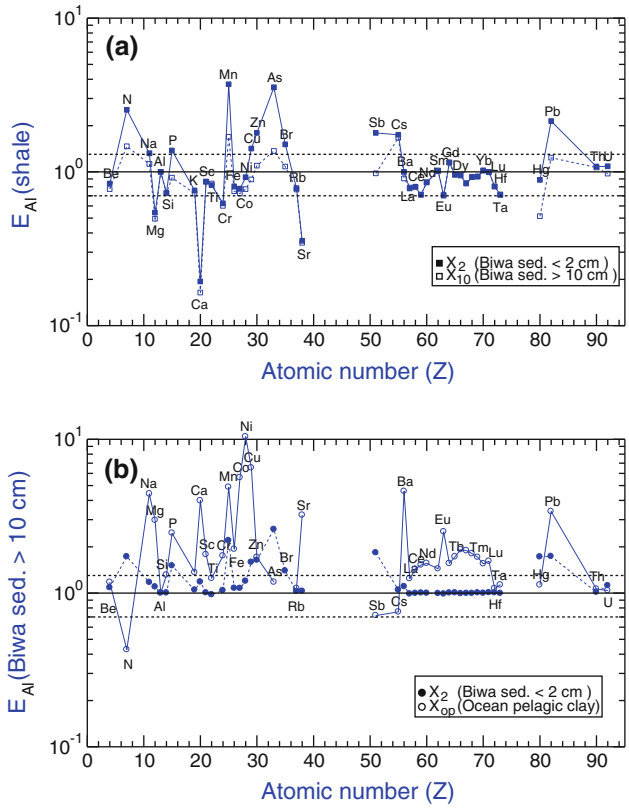

Fig. 4 **a** The enrichment factors of elements (E^i_{Al}) for Lake Biwa sediments at the top 2 cm (X_2) and below 10 cm (X_{10}), as normalized to the world's average shale (X_{sh}), and **b** enrichment factors of elements (E^i_{Al}) for Lake Biwa sediments at the top 2 cm (X_2) and ocean pelagic clay (X_{op}), as normalized to Lake Biwa sediments below 10 cm (X_{10})

to the factor analysis, those enriched elements (excluding P, Ca, REE) are all related to Mn oxide coating of oceanic pelagic clay, whereas P, Ca, and REE are associated with phosphate phases in the pelagic clay (Li 2000; Li and Schoonmaker 2004). As mentioned earlier, the $BaSO_4$ in marine sediments is an additional sink for Ba. Organic matter in the oceanic pelagic clay is too low in content to be a significant sink for those enriched elements. In the plot of log X_2/C_{LB} (log K_d of elements between the Lake Biwa surface sediments and water, or $-\log \tau^*_{LB}$) versus log X_{op}/C_{SW} (log K_d of elements between the oceanic pelagic clay and seawater, or $-\log \tau^*_{SW}$) (Fig. 5), most data points do not fall on the concordant line (solid line in Fig. 5). However, those parameters are more or less linearly correlated (dotted line in Fig. 5). Therefore, the rankings of relative reactivity of elements in Lake Biwa and the ocean are rather similar. The τ^*_{LB} of various elements in Lake Biwa range from 10^{-2} to 10^4 years, whereas τ^*_{SW} in the ocean range from a few to 10^9 years. For A-type alkali and alkaline-earth cations (such as Na, K, Rb, Cs, Mg, Ca, and Sr), log X_{op}/C_{SW} are much smaller than log X_2/C_{LB} (Fig. 5). The implication is that the exchangeable sites in oceanic pelagic clays are already more or less saturated with those ions due to relatively high concentrations of those ions in seawater, and they cannot be the major sink for those ion inputs from rivers. Removal of those ions from the ocean are mainly through the formation of evaporates and carbonate deposits in the ocean (Li 2000). Formation of authigenic clay minerals in ocean sediments by the so-called reverse weathering process (Garrels and Mackenzie 1971) may provide removal mechanism for those ions in the ocean but should be of minor importance. The mid-ocean-ridge hydrothermal vent systems are also important sinks for Mg in seawater (Mottl 1983). In contrast, removal of alkali and alkaline-earth elements from the Lake Biwa water column by adsorption processes should be appreciable. There is no direct evidence of active reverse weathering in Lake Biwa sediments. The observed log $X_{op}/C_{SW} << \log X_2/C_{LB}$ for U (Fig. 5) reflects the formation of stable uranium–carbonate complexes (e.g. $UO_2[CO_3]_2^{2-}$) in seawater. Most B-type ions (Fe, Mn, Co, Pb, Cu, Ni, Zn, As, Sb) and Ba fall on the left of the dotted correlation line, again reflecting the effect of enhanced adsorption of B-type ions and Ba by Mn oxide coating on the deep-sea sediment particles. According to the factor analysis of many oceanic pelagic sediment data, the B-type elements Mn, Co, Pb, Cu, Ni, Zn plus Ba, Mo, and Mg are highly correlated among themselves, whereas Fe, As, and Sb covary whenever there is appreciable hydrothermal input in sediments; otherwise, they mainly associate with aluminosilicate phases (Li and Schoonmaker 2004). Barium also can be partially removed from the ocean by $BaSO_4$ particles, as mentioned earlier. Takebe (2005) showed that REE in the Pacific deep-sea sediments are mainly associated with phosphate phases, such as carbonate–fluorapatite (e.g. $Na_{0.5}Ca_5[PO_4]_{2.5}[CO_3][F, OH]$). In contrast, REE are mostly associated with detritus aluminosilicate phases in Lake Biwa sediments (Li et al. 2007). However, light REE (La, Ce, and Sm) are sometime associated with the weathering-resistant minerals, such as monazite, (Ce, La, Th) PO_4 in the lake sediments.

As shown in Fig. 6, the log K_d of Ce shows large and small positive anomalies (2Ce/(La + Pr) > 1) for the ocean and Lake Biwa, respectively, confirming the oxidative uptake of Ce at the water–solid interface, especially in the ocean (Li 1991). The log K_d for REE heavier than Ce is always lower in the lake than in the ocean, and the

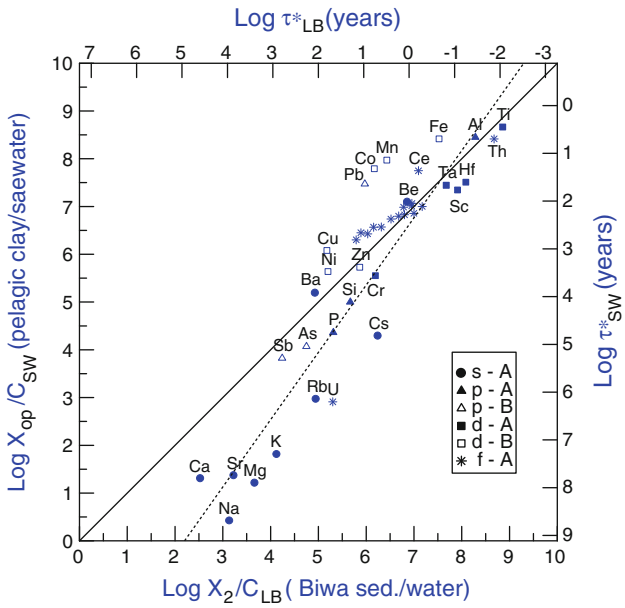

Fig. 5 Plot of log X_2/C_{LB} versus log X_{op}/C_{SW}. Ratios are in units of cm^3/g. *Solid line* is the concordant line

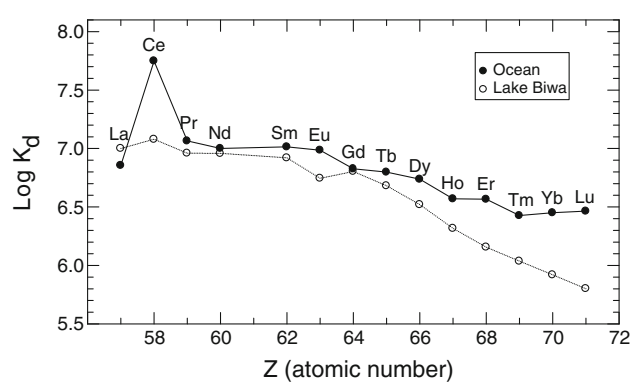

Fig. 6 Logarithms of the distribution coefficient (log K_d) of rare earth elements (REE) between sediments and water in Lake Biwa (*open circles*) and the ocean (*closed circles*) as a function of atomic number (*Z*)

differences become larger after Gd (Fig. 6). The best explanation is again that the complexation constants of REE with organic colloids in the lake and with carbonate ion in seawater increase with atomic number; thus, the total concentrations of dissolved (<0.45 μm) REE increase (Fig. 3) and K_d values decrease with atomic number (Fig. 6).

The plots of log X_{op}/C_{SW} and log X_2/C_{LB} versus I_z in Fig. 7a and b show the similar up-and-down "Λ" relationship. In other words, the systematic variation of log K_d (=log X_{op}/C_{SW} in the ocean, and =log X_2/C_{LB} in the lake) may reflect some degree of adsorption/desorption equilibrium in both systems, and the log K_d value is for the first approximation proportional to the relative bond strength between adsorbing ions and hydrolyzed surface of oxide particles (Li 2000, 2008). The relatively high log X_{op}/C_{SW} and log X_2/C_{LB} values for large-size alkali and alkaline-earth cations, such as K, Cs, Rb, and Ba in Fig. 7a and b, can be in part explained by their relatively low secondary solvation energy. The hydration waters around a large cation are less tightly held. Therefore, a large cation can be easily adsorbed onto solid surface after releasing loosely bound hydration waters (James and Healey 1972). The relatively high log X_{op}/C_{SW} values for Mn, Co, Ce, Pb, and Tl in Fig. 7a reflect additional oxidative uptake of those elements on Mn oxide coating of sediment particles (Li 1991; $Mn^{2+} \rightarrow Mn^{4+}$, $Co^{2+} \rightarrow Co^{3+}$, $Pb^{2+} \rightarrow Pb^{4+}$, $Ce^{3+} \rightarrow Ce^{4+}$, and $Tl^{+} \rightarrow Tl^{3+}$). However, the oxidative uptake of those elements on Lake Biwa sediments is not pronounced (Fig. 7b). As demonstrated by Kawashima et al. (1988), Mn is recycled rapidly through reduction–oxidation processes at the sediment–water interface in the deep Lake Biwa and does not accumulate much in the anoxic subsurface sediments. This is also supported by the fact that the composition of subsurface sediments (X_{10}) is essentially the same as that of the world average shale (Fig. 4a). Mn inputs from rivers end up in oxic surface sediments, Mn crusts, and concretions, and some export out of the lake by river outflows. For elements with asterisk in Fig. 7a and b, such as Tl, Ag, Au, Pb, Hg, and Bi (all d^{10}-cation); Li and Be (smallest ionic radius among alkali and alkaline-earth cations); B, Ti, and U (as oxycations $B[OH]_3^0$, $Ti[OH]_2^{2+}$, and UO_2^{2+}); and F^-, Cl^-, and Br^-; the interpolated effective-electron-binding-energies I_z* are used instead of regular electron-binding energy I_z. Why I_z* values are used and how to obtain them are discussed elsewhere (Li 2008).

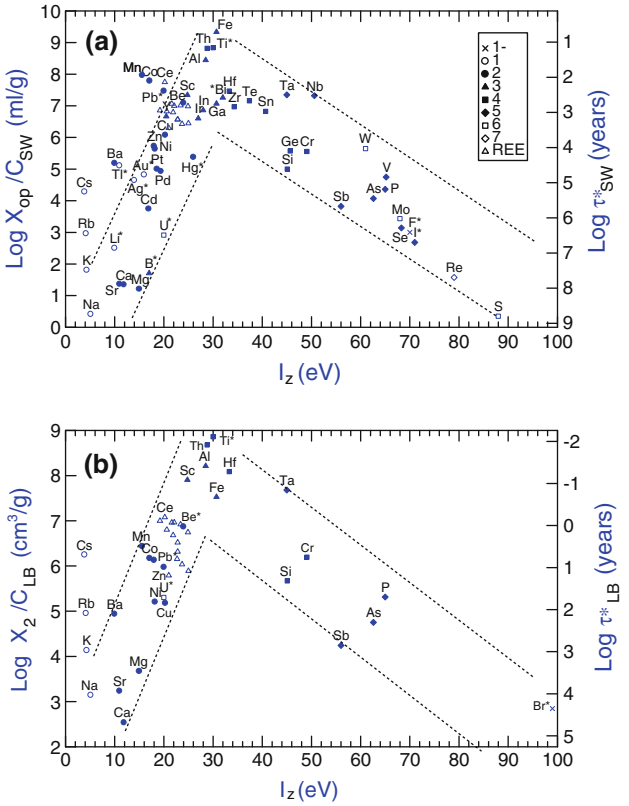

Fig. 7 Plots of I_z (electron-binding energy to gaseous ion with charge z) versus **a** log X_{op}/C_{SW}, and **b** log X_2/C_{LB}. For the *elements with asterisk*, the effective electron-binding energies I_z* are used (for details, see Li 2008)

Manganese crusts and concretions from Lake Biwa

A flat rock pebble collected south of site *Z* (Fig. 1) at a water depth of about 20 m was covered with Mn crusts. The composition of Mn crust on the top and bottom of the pebble (X_t and X_b, respectively, in Table 3) are compared with those of Lake Biwa sediments <10 cm (X_{10}) and are shown in Fig. 8a in terms of the enrichment factor E_{Al}. Elements Be, P, Ca, Mn, Fe, Co, As, Sr, Sb, Ba, and U are all enriched ($E_{Al} \geq 2$) in the Mn crusts compared with Lake Biwa sediments (X_{10}). Furthermore, the enrichment of those elements in the bottom Mn crust (X_b) is always much higher than in the top Mn crust (X_t), indicating additional pore-water sources of those elements for the bottom Mn crust. The elements Cu, Zn, Sr, Cs, REE, and Pb are also enriched but only in the bottom Mn crust, again suggesting pore-water sources. The elements with $0.5 < E_{Al} < 2$ in the Mn crusts (Mg, Al, Si, Sc, Ti, Cr, Br, Rb, Hf, and Th) are mostly contributed by clay particles incorporated into the Mn crusts.

One more Mn crust sample taken from the side of the pebble is similar to the top sample in composition (Takamatsu et al. 1985b). Among these three Mn crust samples (top, side, and bottom) and the average Lake Biwa sediments <10 cm (X_{10}), the concentrations of P, As, Sb, Fe, Co, and Mn covary strongly (with correlation coefficients >0.9 among any pair based on the obtained correlation matrix, not shown here). Mn, Co, Ca, Ba, Cu, Ni, and Zn also covary strongly among themselves. In short, divalent

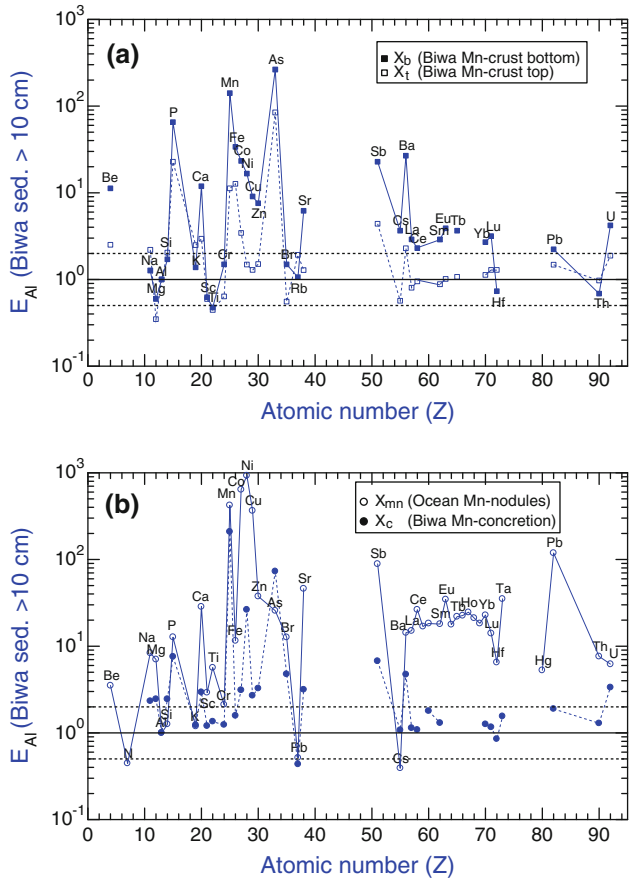

Fig. 8 **a** E^{i}_{Al} for the top (X_t) and bottom (X_b) manganese (Mn) crusts from Lake Biwa; and **b** E^{i}_{Al} for Lake Biwa Mn concretion (X_c) and ocean Mn nodules (X_{mn}); all normalized to the Lake Biwa sediments below 10 cm (X_{10})

cations tend to associate mainly with Mn oxide phases and oxyanions with Fe oxide phases. The appearance of Mn and Co in both Fe and Mn oxide groups indicates that the amounts of Mn and Fe oxide phases are also positively correlated. Apparently, both Fe and Mn are effectively mobilized under highly anoxic conditions in the pore water 0.2–0.3 cm below the sediment–water interface at the sampling site of Mn crust (Takamatsu et al. 1985b). This is not the case for ocean Mn nodules, where the amounts of Mn oxide and Fe oxide phases are inversely correlated (Li 1982; Li and Schoonmaker 2004). Elements Al, Mg, Sc, Ti, Cr, Hf, Pb, and Th are again associated with clay phases in the lake Mn crusts, as indicated by their inverse correlation with the elements that are associated either with Fe or Mn oxide phases.

REE are associated with clay phases within the top and side Mn crusts, but REE in the bottom Mn crust are high and must reside in yet-to-be-identified phases (could be apatite?), which are not related to the Mn and Fe oxide phases. Elements enriched in the bottom Mn crust (X_b) of the lake are even more enriched in ocean Mn nodules (X_{mn}; Fig. 8b). The exceptions are P, Fe, and As, which are much higher in the lake Mn crusts (compare Fig. 8a, b; see Table 3). Apparently, Mn crusts formed in shallow water (~20 m) of the lake had ample dissolved Fe and Mn supplies from nearby reducing sediments, as mentioned earlier, and the precipitation of Fe oxides around Mn crusts incorporated oxyanions such as P and As.

The significant enrichment of Sc, Ti, REE, Hf, Ta, and Th in marine Mn nodules (Fig. 8b) indicates appreciable dissolved (including colloids) sources for those highly particle-reactive elements in the deep marine environments. Based on the factor analysis of ocean Mn nodules data, the major components of Mn nodules include Mn oxides, Fe oxides, carbonate–fluorapatite (CFA), and clay phases (Li 1982; Li and Schoonmaker 2004). Unlike Lake Biwa Mn crusts, the amounts of Mn and Fe oxide phases are inversely correlated in ocean Mn nodules, as mentioned earlier. Mn oxide phases concentrate mono- and divalent cations with low to moderate first hydrolysis constant values (such as Tl, Ag, Mg, Ba, Ni, Cu, Cd, and Zn) and oxyanions of Mo and Sb. Fe oxide phases concentrate tri- to penta-valent cations that exist in normal seawater as hydroxyl and carbonate complexes (e.g., B, Bi, In, Ir, Rh, REE, Y, Ti, Th, U, Zr, Hf, Nb, and Ta), oxyanions (As, P, Re, Ru, Os, S, Se, Te, V, and W), and divalent cations with high first hydrolysis constants (such as Hg, Be, Pd, Co, and Pb). CFA is closely associated with Fe oxide phases and contributes significant amounts of Ca, Sr, P, C, REE, and Y. Elements Al, Si, K, Na, F, Cr, Rb, Cs, Sc, Ga, Sn, and Ge in ocean Mn nodules are again mainly contributed by clay phases.

The friable Mn concretions grown on surface sediments of Lake Biwa (X_c in Table 3) were collected at site *G* (Fig. 1) at a water depth of about 97 m. Its average composition is similar to that of the top Mn crust (X_t), except that Fe and Co are not as greatly enriched (compare Fig. 8a, b), probably indicating scarcity of dissolved Fe and Co sources in deep Lake Biwa where the redox potential may not be low enough to reduce Fe and Co oxides into dissolved cations. Elements with E_{Al} <1.5 (including Al, Si, K, Sc, Ti, Cr, Fe, Rb, Cs, REE, Hf, Ta, and Th) in Mn concretions (Fig. 8b) are again mostly contributed by clay particles in the Mn concretions.

As shown in Fig. 9a and b, the log X_{mn}/C_{SW} and log X_b/C_{LB} versus I_z again show a general "Λ" relationship, indicating the importance of some degree of chemical equilibrium between solid phase (Mn nodules in the ocean, X_{mn}, or the bottom Mn crust in Lake Biwa, X_b) and liquid phase (seawater, C_{SW} or Lake Biwa water, C_{LB}). The significantly high log X_{mn}/C_{SW} values for Mn, Co, Ce, Pb, and Tl in Fig. 9a again reflect additional oxidative uptake of those elements on the surface of marine Mn nodules (Li 1991, 2000, 2008). The oxidative uptake of those elements

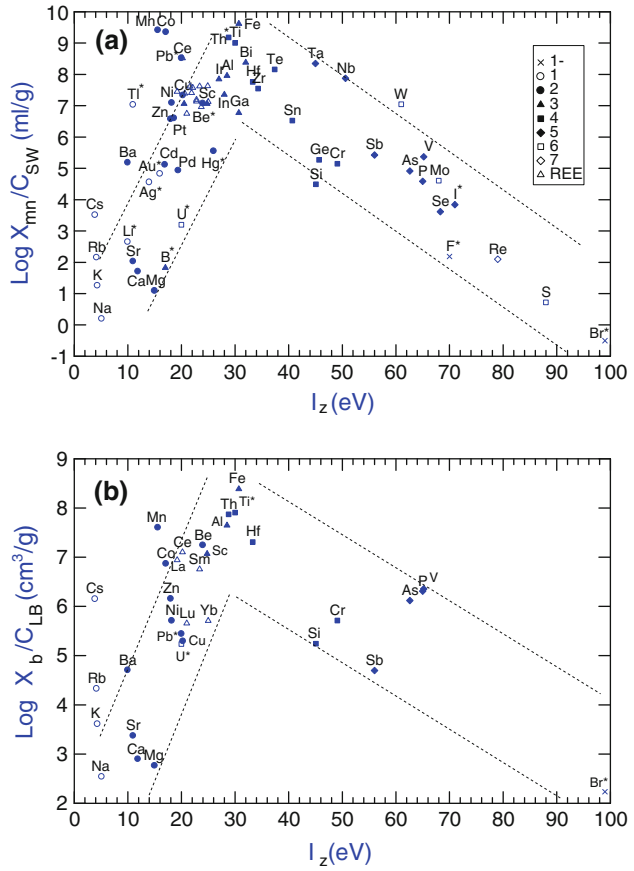

Fig. 9 Plots of I_z (electron-binding energy to gaseous ion with charge z) versus **a** log X_{mn}/C_{SW}, and **b** log X_b/C_{LB}. For the *elements with asterisk*, the effective electron-binding energies I_z* are used (for details, see Li 2008)

(excluding Mn) in Lake Biwa Mn crusts is again not as pronounced (Fig. 9b). The high log K_d values for Cs, Rb, and Ba in Fig. 9a and b again can be attributed to their low secondary solvation energy. The high log X_{mn}/C_{SW} for W in Fig. 9a may result from overestimation of the average W concentration in ocean Mn nodules. Future validation is needed.

Summary and conclusions

1. For A-type ions more concentrated than Cr in seawater, the average dissolved concentrations tend to be much higher in seawater than in Lake Biwa (Fig. 2), corresponding to their relatively long mean residence times (>10^4 years) in the ocean. The average dissolved concentrations of B-type ions tend to be lower in seawater than in the lake due to effective removal of those elements by Mn oxide coating on the oceanic pelagic clay particles.
2. The average composition of Lake Biwa core samples 10 cm below core top (X_{10}) is similar to that of the world's average shale (X_{sh}), except for Mg, Ca, and Sr, which are much lower (Fig. 4), due to preferential leaching during weathering process. The core-top 2-cm sediment samples (X_2) have higher concentrations of N, P, Mn, Cu, Zn, As, Br, Sb, Hg, and Pb than those of X_{10}. Those enriched elements are associated mainly with organic matter and Mn oxide phases in the surface sediments.
3. For A-type alkali and alkaline-earth cations (excluding Be and Ba), log X_{op}/C_{SW} values are much smaller than log X_2/C_{LB} (Fig. 5). The implication is that the adsorption sites in oceanic pelagic clays are already saturated with those cations due to relatively high concentrations of those cations in seawater, and cannot be the major sink for those cation inputs from rivers. Log X_{op}/C_{SW} tend to be higher than log X_2/C_{LB} for B-type ions, Ba, and heavy REE, again reflecting the effect of enhanced adsorptive removal of B-type ions and Ba by Mn oxide coating on the deep-sea sediment particles. Ba is also removed by $BaSO_4$ particles. The removal of heavy REE are mainly associated with phosphate phases in the deep-sea sediments. In comparison, REE are mostly associated with aluminosilicate phases in the Lake Biwa sediments, and the light REE (La, Ce, and Sm) are sometime associated with the weathering-resistant minerals such as monazite ([Ce, La, Th]PO_4).
4. The REE variation patterns of log (C_{LB}/X_{sh}) and log (C_{SW}/X_{sh}) in Fig. 3 and log (X_2/C_{LB}) and log (X_{op}/C_{SW}) in Fig. 6 suggest the following: The much larger positive Ce anomaly in the deep-sea sediments than in the lake sediments reflects oxic environment of the deep-sea surface sediments (at least 20- to 40-cm thick) compared with that of Lake Biwa (only 0.2–0.3 cm). The carbonate complexes of REE are important species in the ocean. In contrast, REE form strong complexes with large and small molecule weight organic colloids in the Lake Biwa water column.
5. Elements Be, P, Ca, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Sb, Ba, REE, Pb, and U are all enriched in the lake Mn crusts compared with the lake sediments (Fig. 8a). The enrichment of those elements in the bottom Mn crust (X_b) is always much higher than in the top Mn crust (X_t). The average composition of friable Mn concretions (X_c) is similar to that of the top Mn crust. The elements that are enriched in the bottom Mn crust are even more enriched in the ocean Mn nodules (X_{on}), except for P, Fe, and As, which are higher in the Mn crusts of the lake. Apparently, Mn crusts formed in shallow water (~20 m) of the lake had ample dissolved Fe, P, and As supply from nearby reducing sediments.

6. The up-and-down "Λ" relationship for log X_2/C_{LB}, log X_t/C_{LB}, log X_{op}/C_{SW}, and log X_{mn}/C_{SW} as a function of I_z (electron-binding energy to gaseous ion with charge z; Figs. 7, 9) are consistent with the surface complexation model. In other words, the systematic variation of log K_d with I_z reflects some degree of adsorption/desorption equilibrium, and the log K_d value is, for the first approximation, proportional to the relative bond strength between adsorbing ions and hydrolyzed surface of oxide particles.

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