

A selective chemical leaching study of sediments from fresh-water lake, brackish-water lake and sea in the Japan areas

Yutaka KANAI*

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Abstract : The selective chemical leaching method was applied to recent surface sediments from fresh-water lakes, brackish-water lakes in Japan and sea around Japan. Chemical composition of each fraction was determined and relationships among samples and elements were examined.

The majority of Na dissolved in the water-soluble fraction. Most elements showed the tendency of $C(B), C(S) > C(F)$ except for Mn, Rb and Ba, where $C(B), C(S), C(F)$ are average concentrations of samples from brackish-water lakes, from sea, from fresh-water lakes, respectively. $AcONH_4$ soluble fraction of Fe, Mn, Al and Ba showed $C(F) > C(B), C(S)$. This may be ascribed to the original water composition around the sediments. $AcOH$ soluble fraction is important for carbonate forming elements, and Fe showed the trend of $C(F) > C(S)$ as expected from seawater / river water ratio. $NH_2OH \cdot HCl$ soluble fraction was mainly composed of Fe, and many metal ions were also detected in this fraction.

The relationship among $C(F), C(B)$ and $C(S)$ was shown to depend mainly on the seawater / river water ratios and each chemical condition. It also depends on mineral type, degrees of weathering and alteration, grain size, surface form, and surface coating matrix. More case studies will be necessary to testify the relationship in detail.

1. Introduction

A selective chemical leaching method was first applied to the pelagic sediments by Goldberg and Arrhenius (1958). This method aimed to separate the elements by their states and characteristics, and to elucidate the authigenic minerals and how the elements attached or adsorbed to the sediment grains.

They used cellophane, 1M ammonium acetate and EDTA (ethylene diamine tetra acetic acid), and later Chester and Hughes (1967) used 1M hydroxylamine and 25% acetic acid mixture. Then various reagents and techniques have been proposed by Plesley *et al.* (1972), Aghayan and Chau (1976), Farrah and Pickering (1978), Kitano and Fujiyoshi (1980). Some methods are

keywords : selective chemical leaching, state analysis, surface sediment, sedimentary environment, lake sediment, sea sediment

* Geochemistry Department

reviewed by Kanai (1993).

Most studies are concerned about oceanic sediments, and few studies have been achieved about lake or brackish water sediments. As this technique is useful to clarify the state and condition of the elements in sediments, it may give a clue to elucidate the paleo-environment of sedimentation. Kanai (1986) studied the relationships between the sedimentation depth and the chemical composition obtained using the selective chemical leaching method. He found the importance and usefulness of this technique.

The purpose of this study is to apply the selective chemical leaching technique to the recent surface sediment samples deposited

under fresh-water, brackish-water and sea-water, and to clarify the differences and relationships of the chemical composition among samples and fractions.

2. Samples and experimental

Thirty-three samples were collected from fresh-water lakes (11 samples), brackish-water lakes (7 samples) in Japan, and sea around Japan (15 samples). The sampling locations are shown in Fig. 1 and listed in Table 1. Most of the samples were collected from 50-200 cm below the sediment-water interface. They were dried in the air, powdered slightly, and subject-

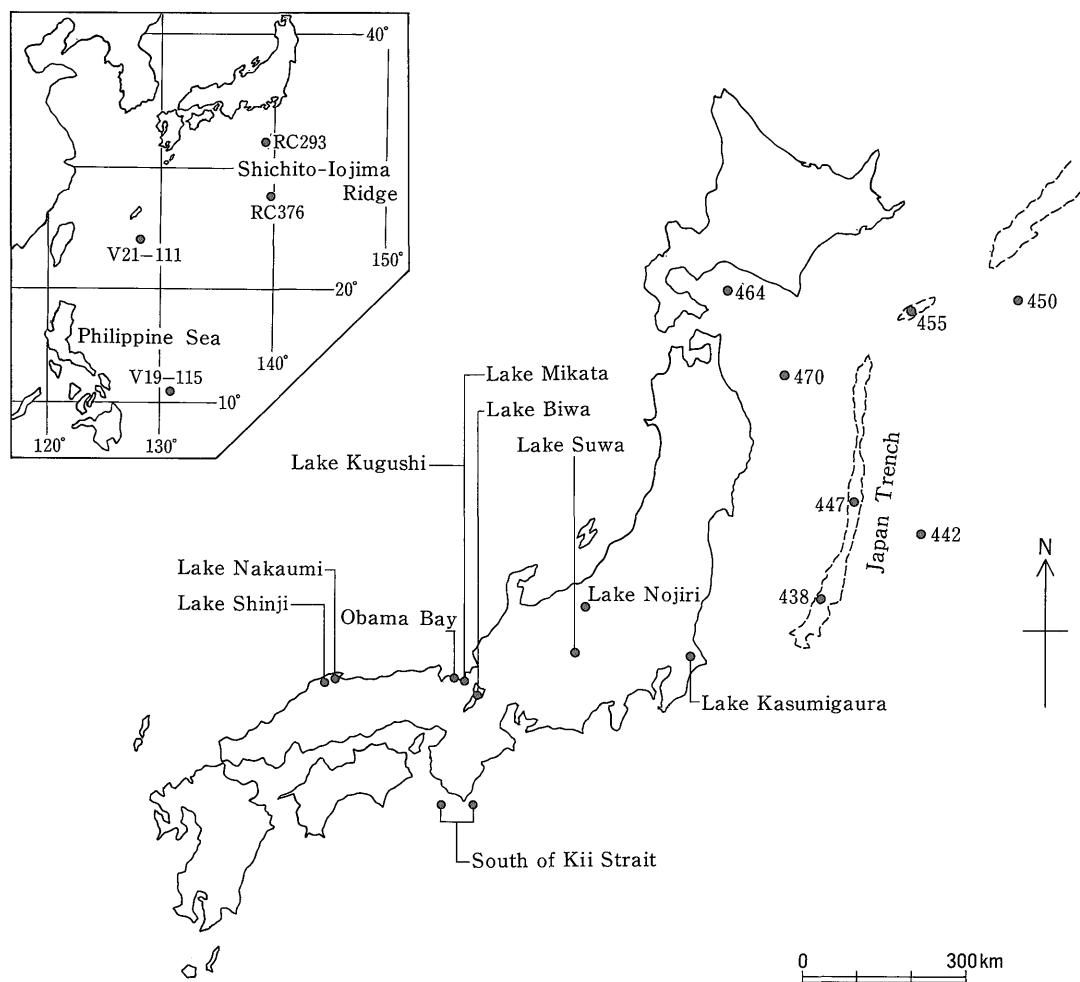


Fig. 1 Sampling locations of sediments.

ed to the following selective chemical leaching process.

Although leaching technique is really a unique method, the interpretation is rather complicated because the reagents used by each researcher are different little by little and the reagent is not at all specific to only one mineral. For example, in order to leach exchangeable ions, Goldberg

and Arrhenius (1958), Kitano and Fujiyoshi (1980) used AcONH_4 , while Tessier *et al.* (1979) used MgCl_2 . The former reagent may attack some amount of carbonate (Tessier *et al.*, 1979) and the latter reagent cannot be used for the Mg determination. So, it should be mentioned which reagents and conditions were used in the leaching experiment, and each fraction should be

Table 1 Samples and sampling locations of sediments.

no.	sampling location		depth	latitude	longitude
< fresh-water >					
F- 1	Lake Nojiri	P-2*,	55- 60 cm	below the bottom	
F- 2	Lake Nojiri	P-4,	50- 51 cm		
F- 3	Lake Nojiri	P-4,	80- 80 cm		
F- 4	Lake Suwa	St-2,	60- 75 cm		
F- 5	Lake Suwa	St-2,	80-101 cm		
F- 6	Lake Kasumigaura	St-125,	109-114 cm		
F- 7	Lake Kasumigaura	St-125,	139-144 cm		
F- 8	Lake Biwa	BW-2,	104-109 cm		
F- 9	Lake Biwa	BW-2,	194-199 cm		
F-10	Lake Mikata	St-1,	100-110 cm		
F-11	Lake Mikata	St-1,	120-130 cm		
< brackish-water >					
B-12	Lake Kugushi	St-2,	50- 60 cm		
B-13	Lake Kugushi	St-2,	60- 70 cm		
B-14	Lake Shinji	840811-2,	60- 65 cm		
B-15	Lake Shinji	840811-2,	80- 85 cm		
B-16	Lake Shinji	840811-2,	95-100 cm		
B-17	Lake Nakaumi	St-F,	40- 65 cm		
B-18	Lake Nakaumi	St-F,	70- 80 cm		
< seawater >					
S-19	Obama Bay	IV-5,	surface		
S-20	Obama Bay	VI-5,	surface		
S-21	South of Kii Strait	334,	244-253 cm	33° 23.7 ' N	134° 58.1 ' E
S-22	South of Kii Strait	318,	196-205 cm	33° 14.7 ' N	135° 53.0 ' E
S-23	Off Northeast Japan	464,	127-132 cm	42° 10.0 ' N	141° 41.6 ' E
S-24	Off Northeast Japan	470,	110-120 cm	40° 40.7 ' N	142° 47.0 ' E
S-25	Around the Japan Trench	450,	198-202 cm	41° 37.3 ' N	147° 54.2 ' E
S-26	Around the Japan Trench	442,	172-185 cm	37° 51.0 ' N	145° 35.4 ' E
S-27	Around the Japan Trench	455,	160-180 cm	41° 31.1 ' N	145° 40.9 ' E
S-28	Around the Japan Trench	438,	180-195 cm	36° 42.7 ' N	143° 13.0 ' E
S-29	Around the Japan Trench	447,	198-202 cm	38° 25.8 ' N	144° 05.6 ' E
S-30	Shichito-Iojima Ridge	RC293,	surface	32° 47.9 ' N	139° 34.7 ' E
S-31	Shichito-Iojima Ridge	RC376,	surface	27° 59.6 ' N	140° 39.7 ' E
S-32	Philippine Sea	V21-111,	surface	24° 30.0 ' N	128° 31.0 ' E
S-33	Philippine Sea	V19-115,	surface	11° 20.0 ' N	131° 03.0 ' E

*names of location are from Terashima *et al.* (1986)

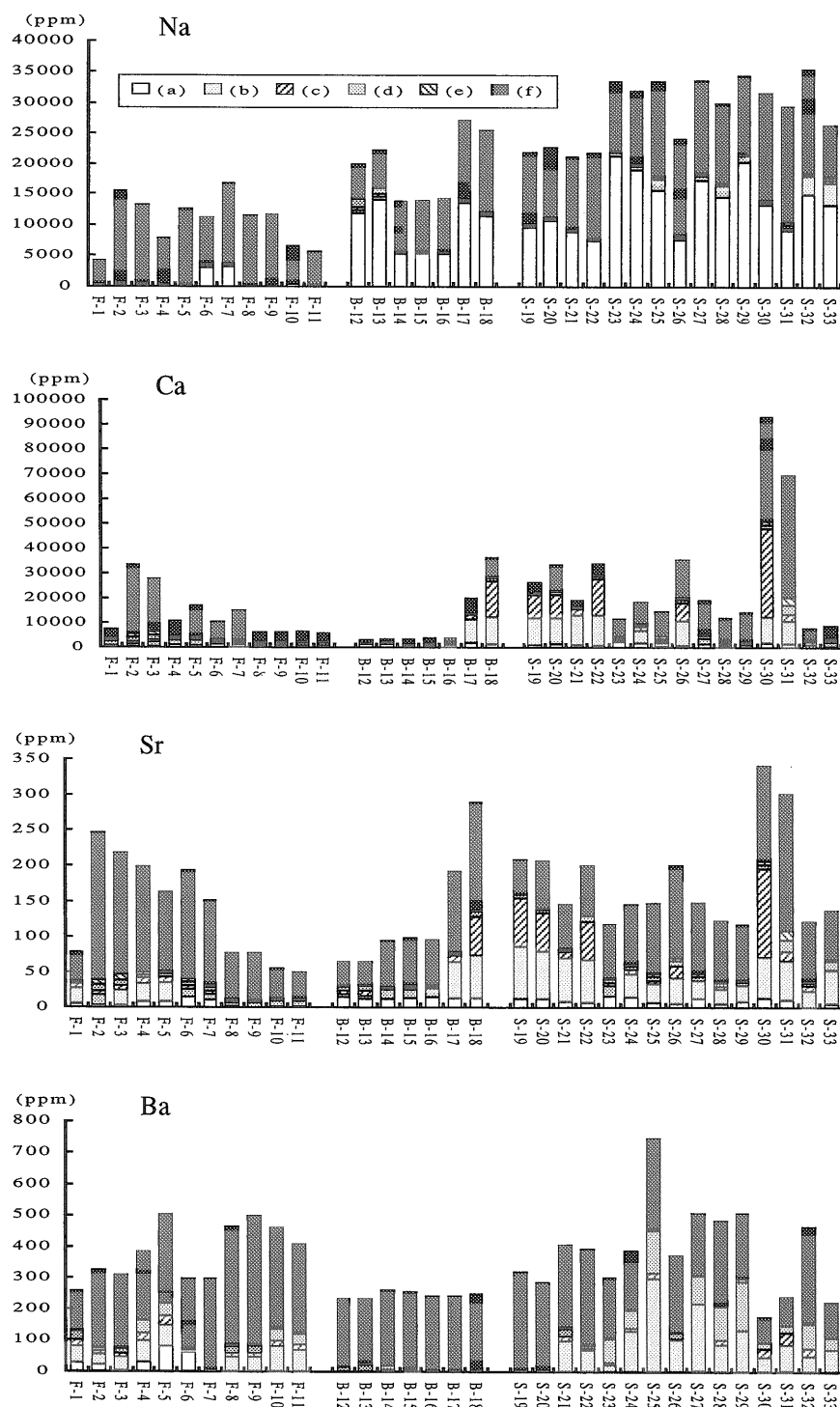


Fig. 2 Elemental concentrations in each fraction. : (a) wash fraction ; (b) AcONH₄ soluble fraction ; (c) AcOH soluble fraction ; (d) NH₂OH·HCl soluble fraction ; (e) H₂O₂ soluble fraction ; (f) silicate fraction ; (g) bulk composition. F-1 to F-11, B-12 to B-18 and S-19 to S-33 are fresh-water lake samples, brackish-water lake samples and sea samples, respectively.

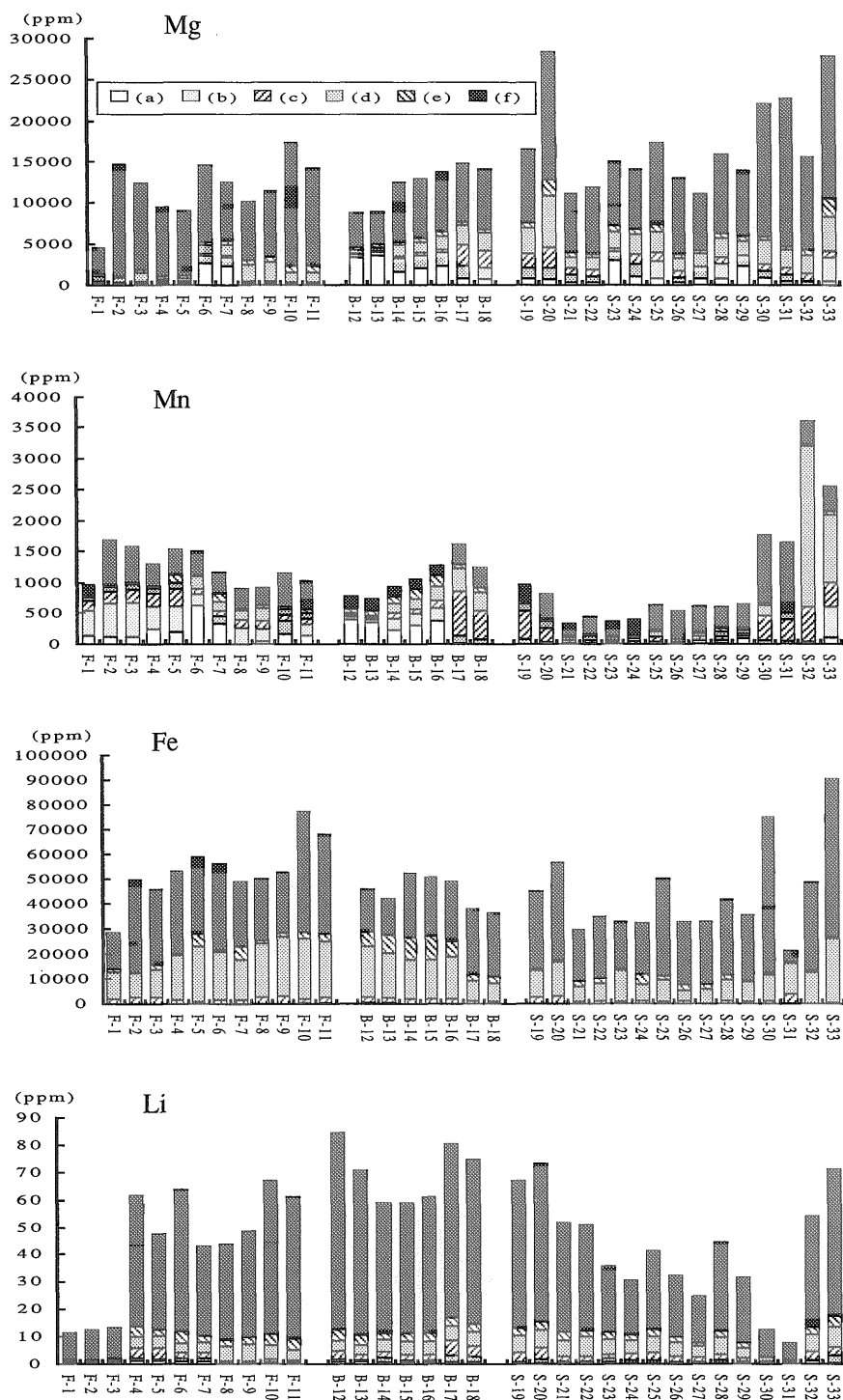


Fig. 2 (Continued)

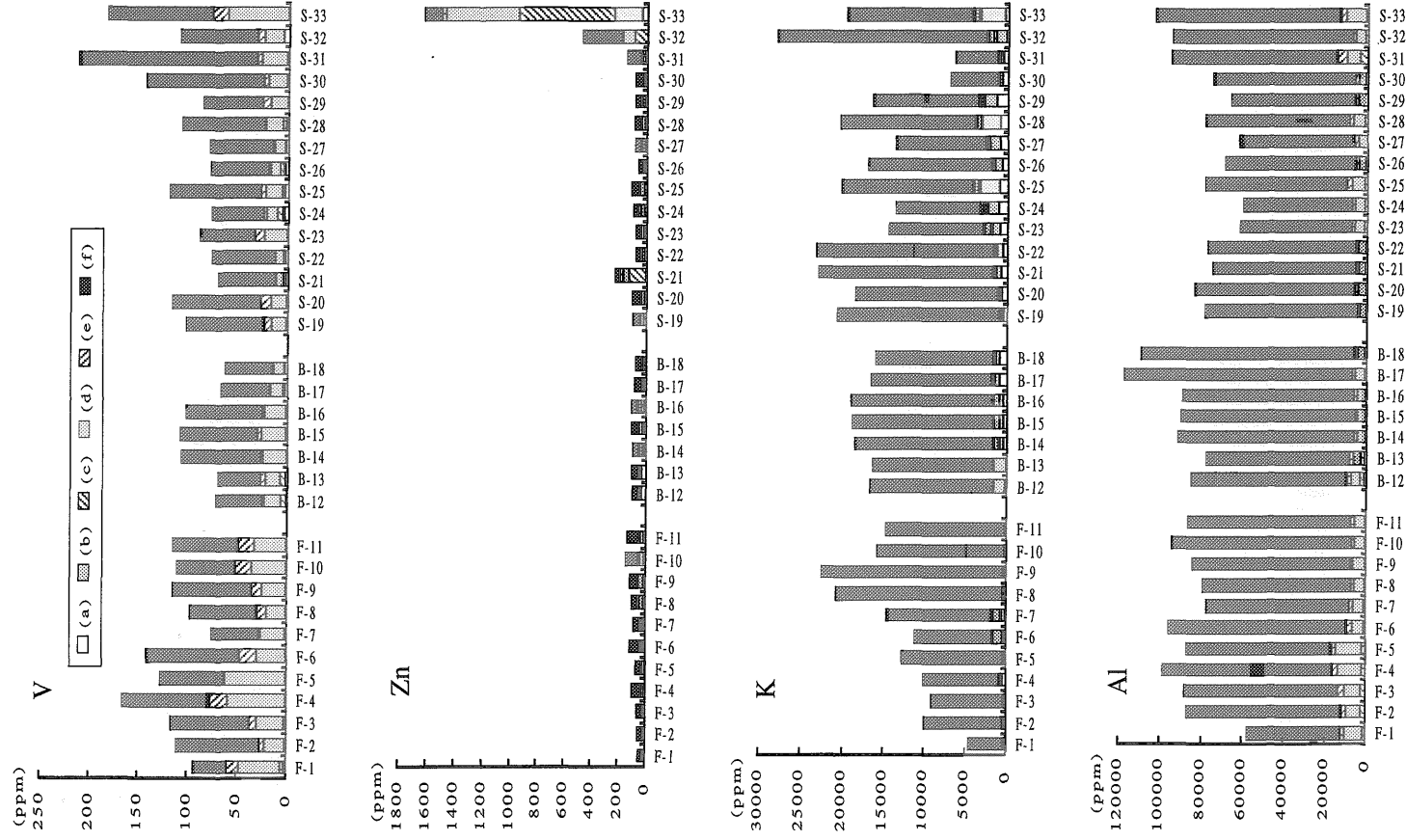


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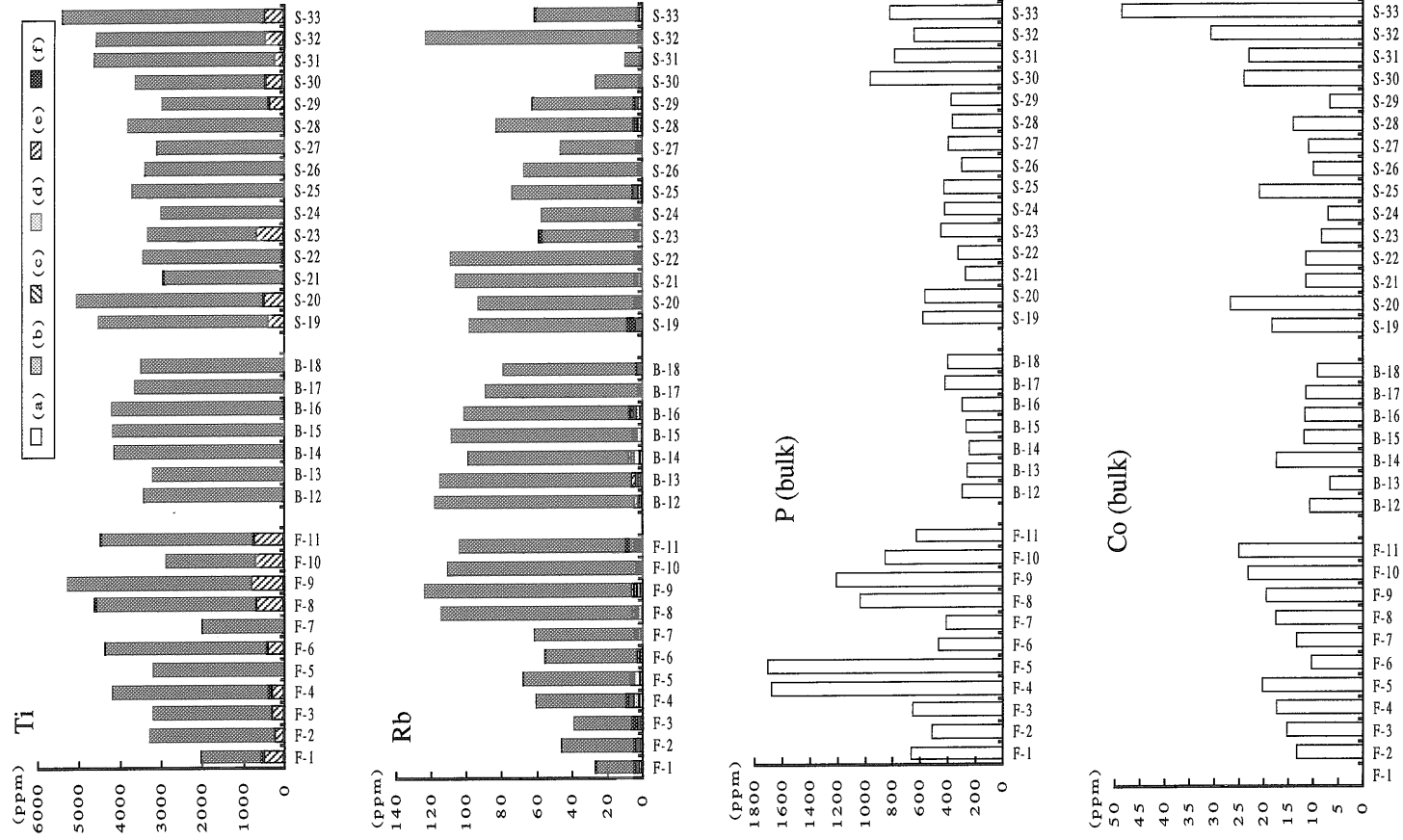


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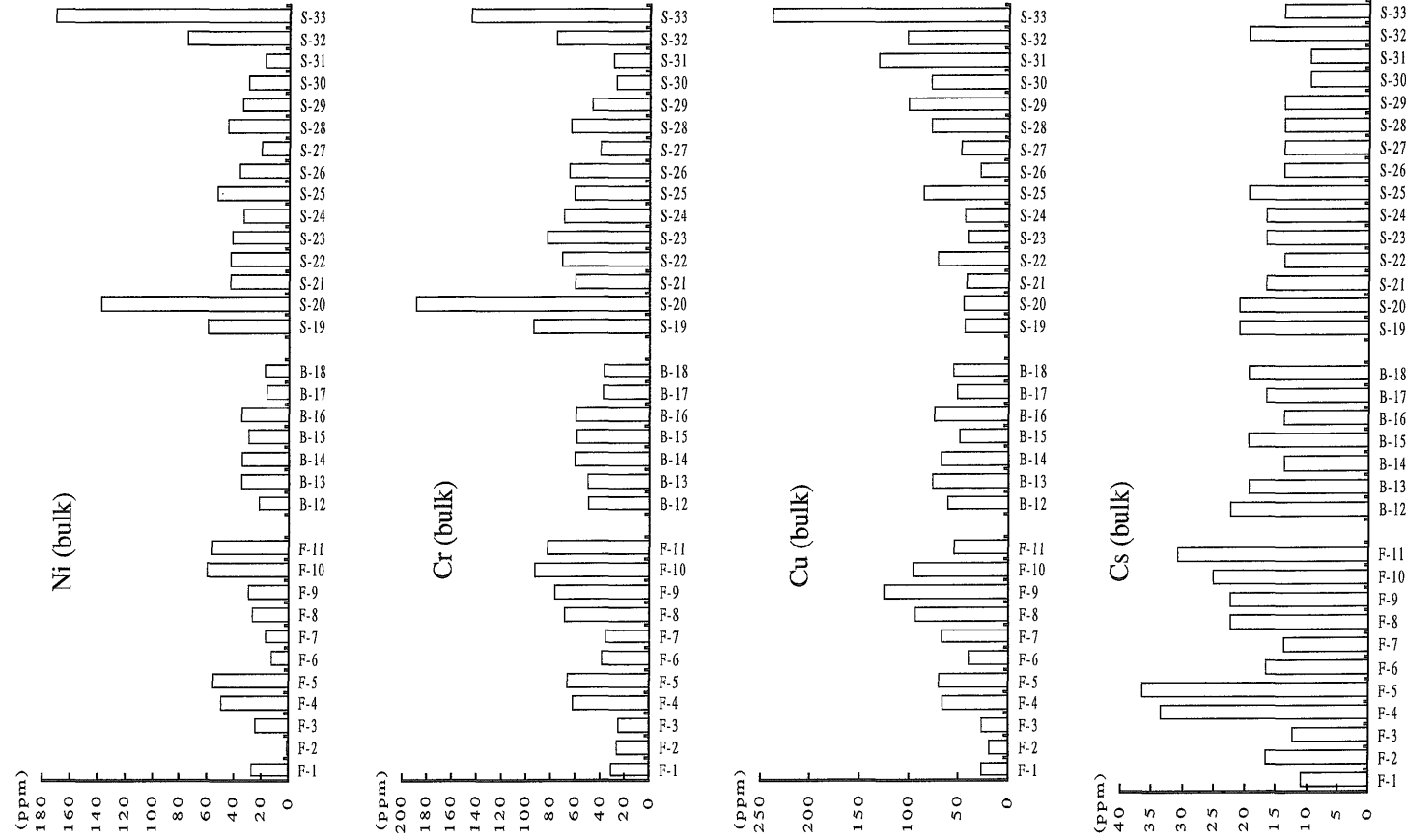


Fig. 2 (Continued)

denoted by the reagent. Malo (1977) compared four methods of partial extraction and proposed to employ 0.3M HCl solution. Although this method is simple, it provides less information of sediments. In this study, the extraction procedure was a little modified after Kitano and Fujiyoshi (1980), and Itoh (1981). The sediment samples were subjected to leaching treatment for one week instead of a half or 3 days.

After dried at 110°C, 1g of sample was weighed immediately. Then it was mixed with 10 ml of deionized water and filtered using 0.45 μ m membrane filter after 10 minutes stand. Repeat this step 5 times, collect filtrate, add a little amount of nitric acid and evaporate to dryness. Then dissolve with hydrochloric acid and determine 20 elements by atomic absorption spectrometry (Na, K), atomic emission spectrometry (Li, Rb, Cs) and ICP (Fe, Al, Mn, Zn, Cu, Cr, Co, Ti, Ba, Ni, V, P, Ca, Sr, Mg). This fraction is called "wash fraction".

Washed residue was put in a flask with 25 ml of 1 M ammonium acetate (AcONH₄) for 1 week at room temperature, and then filtered and washed with water. Add a little amount of nitric acid to the filtrate, evaporate to dryness, dissolve with HCl and analyze as well. This fraction is called "AcONH₄ soluble fraction".

In the same way, the residue was treated with 25 ml of 2.5% acetic acid (AcOH), 25 ml of 1M hydroxylamine hydrochloride (NH₂OH · HCl) and 25% AcOH mixture, and 25 ml of 30% hydrogen peroxide (H₂O₂). Each filtrate fraction is called "AcOH soluble fraction", "NH₂OH · HCl soluble fraction", "H₂O₂ soluble fraction", respectively. The last residue was decomposed with HNO₃, HClO₄ and HF, and called "silicate fraction". Another 1 g of the same sample was taken and analyzed as "bulk composition". The bulk contents for Fe, Al, Mn, Zn, Ti, Ba, V, Ca, Li, Sr, Rb, K, Mg and Na were in good accordance with the sums of each fraction almost within 10% error. The sums for Cu, Cr, Co, Ni, P and Cs disagreed with the bulk contents, because the fractional contents were low and erroneous. Therefore, only bulk composition data for these elements were shown in this study.

3. Results and discussions

3.1 Elemental concentrations in each fraction

The elemental concentrations in each fraction are listed in the Appendix table and shown in Fig. 2. The samples are numbered sequentially and divided into three groups; No. 1 to 11 are from fresh-water, 12 to 18 are from brackish-water, and 19 to 33 are from seawater. The water composition plays an important roll in controlling the diagenesis of the sediments. In situ water chemistry is not known, so the river water data was used as an analogy of fresh-water lake chemistry. The ratios of elemental concentrations in seawater to those in river water are shown in Fig. 3. The data are cited from Tsunogai and Noriki (1983). To study the relationship among groups, the concentration should be discussed using the group average, as each concentration in a group is scattered a little by the sample location. The difference among the group average was examined by t-test. The results in each fraction and element are shown in Table 2. The marks indicate that the averages of two groups are not equal at 98% confidence (<<or>>) or 90% confidence (<or>). The order of elements in Table 2 is the same as Fig. 3, i.e., increasing order of the ratio of content in seawater to in river water.

Wash fraction

The first washing procedure was achieved to remove the effect of interstitial water remained at the time of sampling. Apparently, The alkaline metal ions such as Na and alkaline earth metal ions such as Mg, Ca and Sr, dissolved in this fraction. In particular, Na in the samples from brackish-water lakes and sea dissolved almost half of the total amount. This is really contributed from the remained seawater. On the contrary, the amount of Mn extracted in this fraction was relatively large for the samples from fresh- and brackish-water lakes. Fig. 3 shows that river water (fresh-water) contains manganese ion about thirty times as much as seawater. Therefore, the difference of Mn concentrations in wash fraction is ascribed to the remained water.

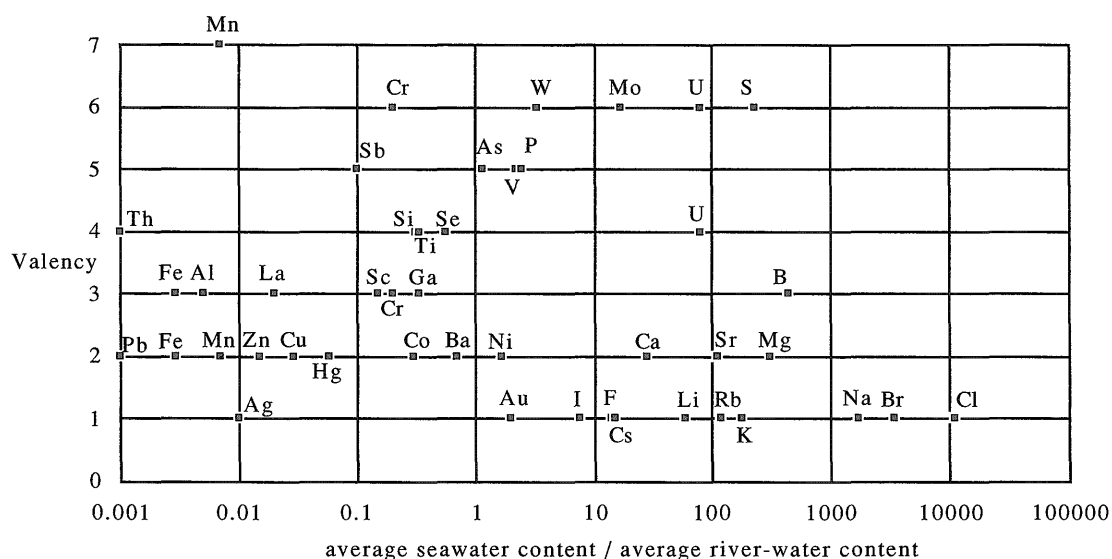


Fig. 3 Ratios of elemental concentrations in seawater to in river water.

Table 2 Relationships among samples from fresh-water, brackish-water, and seawater in each fraction.

fraction		Fe	Al	Mn	Zn	Ti	Ba	V	Ca	Li	Sr	Rb	K	Mg	Na	
1. Wash	fresh		<<		<		>		<<		<<		<	<	<<	brackish
	fresh			>>			>	<<			<	>	<<		<<	seawater
	brackish		>>	>			<<			>>	>>			>		seawater
2. AcONH ₄	fresh			>>			>>			<<				<<	<<	brackish
	fresh	>	>>	>>			<		<<	<<	<<		<<	<<	<<	seawater
	brackish		>				<<						<<		<	seawater
3. AcOH	fresh						>>			<						brackish
	fresh	>							<		<		<<	<<	<<	seawater
	brackish						<<						<<			seawater
4. NH ₂ OH	fresh		>>			>>	>>						<			brackish
	fresh	>>	>				<	>		<				<<		seawater
	brackish						<<		<					<		seawater
5. H ₂ O ₂	fresh	<<	>>	<		>>	>>	>>	>>		>		<<			brackish
	fresh							>								seawater
	brackish	>>		>>			<<	<<	<	<<	>>	<	>		<	<<
6. Silicate	fresh	>		>>						<<				>		brackish
	fresh														<<	seawater
	brackish	<	>	<<					<	>>	<<			<<	<<	seawater
0. Bulk	fresh					>		>>		<<		<	<		<<	brackish
	fresh		>						<		<			<<	<<	seawater
	brackish					<<		<	<<	>>	<	>>		<	<	seawater

<< or >> : averages are not equal to each other at 98% confidence by t-test
 < or > : averages are not equal to each other at 90% confidence by t-test

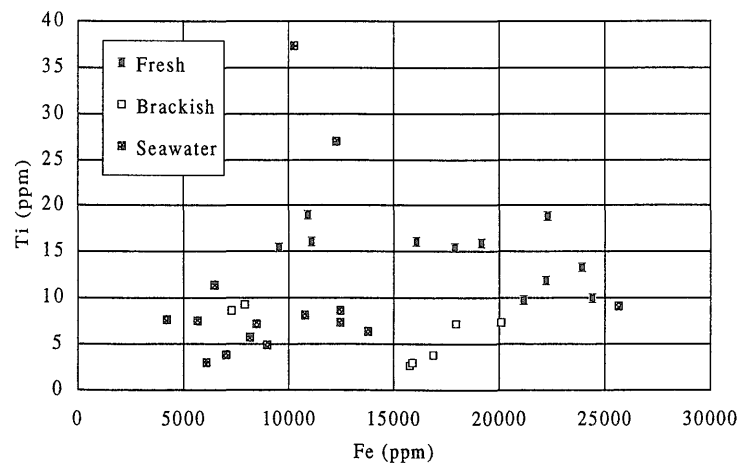
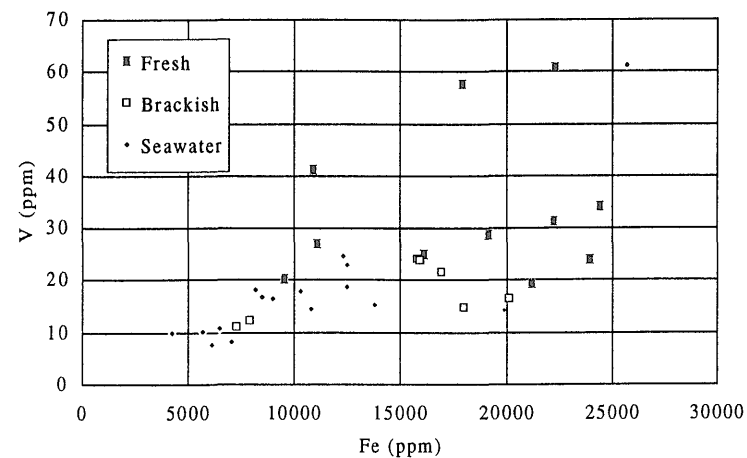
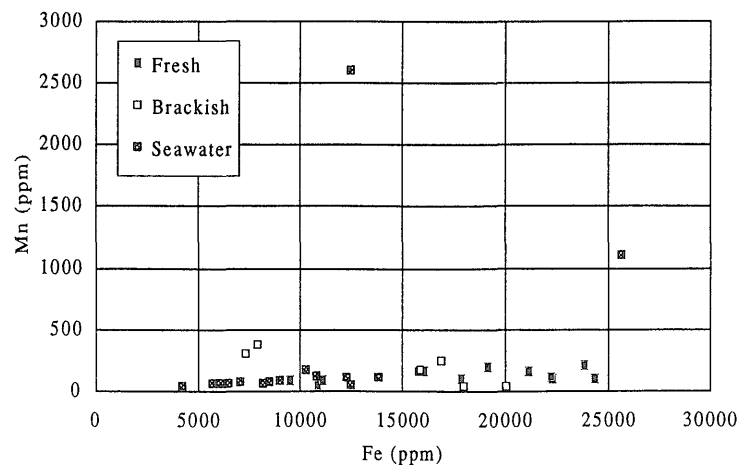


Fig. 4 Relationships among Fe, Mn, Ti and V in $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction.

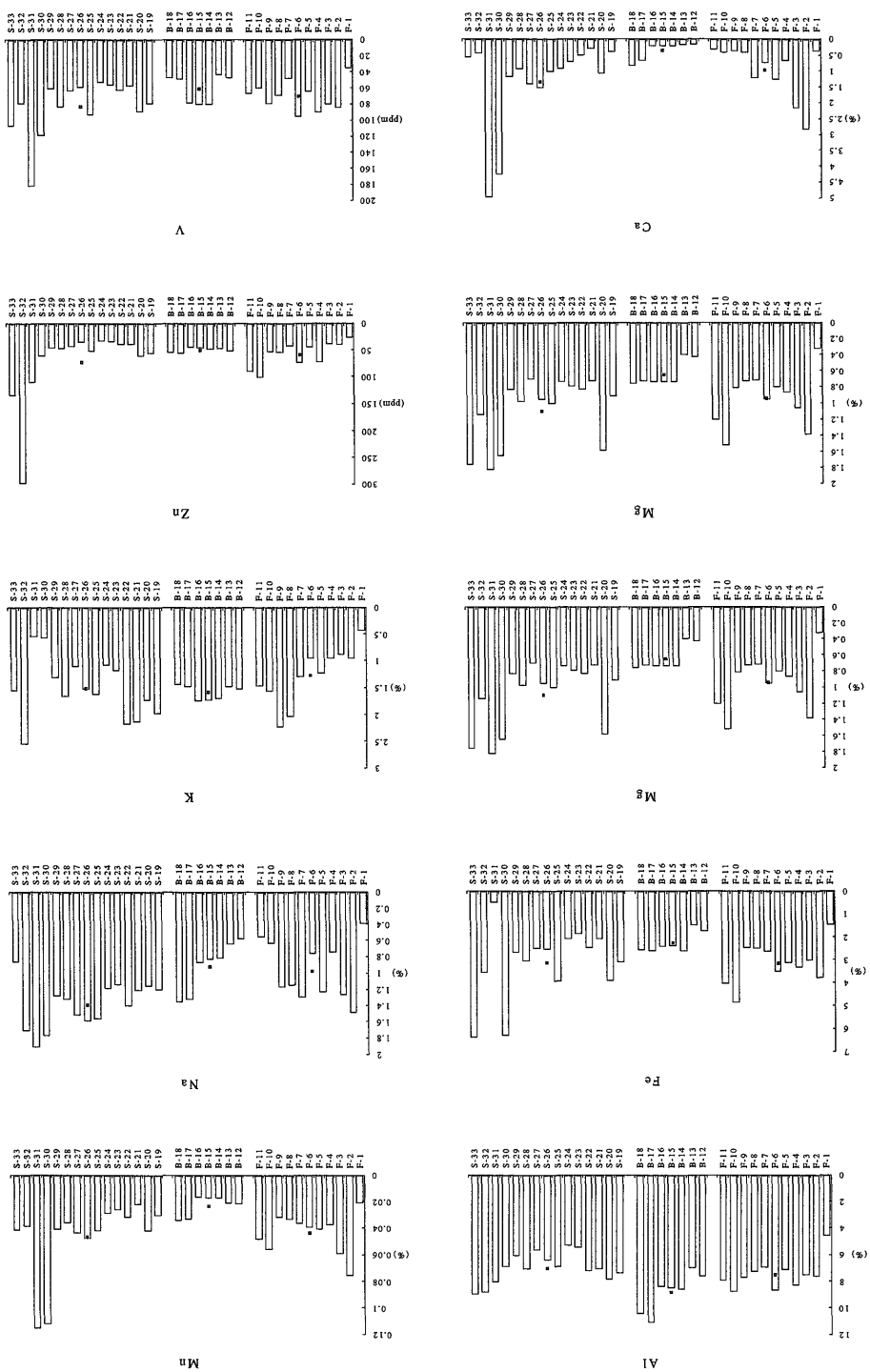


Fig. 5 Concentrations of silicate fractions ; * shows the averages of groups of samples from fresh-water lakes, brackish-water lakes, and sea.

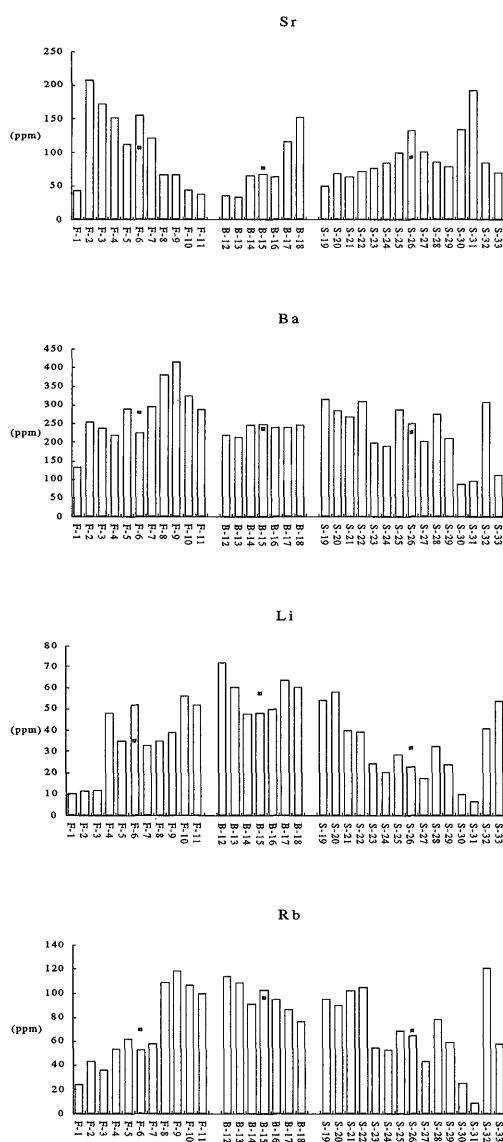


Fig. 5 (Continued)

Among three groups, many elements measured in this study showed the tendency of $C(F) < C(B)$, $C(S)$ except for Mn, Rb and Ba, where $C(F)$, $C(B)$ and $C(S)$ indicate the average concentrations of fresh-water lake samples, brackish-water lake samples and sea samples, respectively. Above tendency might reflect the chemical composition of interstitial water.

AcONH₄ soluble fraction

In AcONH₄ soluble fraction, Fe, Mn, Al and

Ba showed the tendency of $C(F) > C(B)$, $C(S)$. Ions in AcONH₄ soluble fraction are considered to be ion exchangeable. The ion exchange selectivity depends on the properties of interstitial water, such as chemical composition, temperature, pressure, ionic strength, and pH. The seawater is about 3.5% NaCl solution and its ionic strength is about 0.7, higher than that of fresh-water. The pH of seawater is about 8.2, much higher than that of average lake water. The differences mentioned above may explain the observed tendency of the elemental concentrations in this fraction.

AcOH soluble fraction

For AcOH soluble fraction, most elements except Fe and Ba were abundant in the seawater samples. AcOH soluble fraction is thought to relate mainly with the carbonate. Although no fossil was seen in the samples, little carbonate shell might have existed as well as authigenic carbonate minerals. There exist both marine shells and non-marine shells. So, the leached metal concentration might depend on the content of carbonate shells in the sample.

The abundances of minor elements in the carbonate shell are expected to be proportional to the concentration in the water around the shell because the partition coefficient of element between water and solid is almost constant. This may be demonstrated for Fe. Seawater is poor in Fe than river water (Fig. 3), and Fe showed the relationship of $C(S) < C(F)$. However, any linear relationship was not observed between Ca content and metal content except Sr. A further study will be needed because detailed study of the shell has not been conducted.

NH₂OH · HCl soluble fraction

NH₂OH · HCl soluble fraction is thought to be composed of mainly Fe, Mn oxide as insoluble oxide was reduced to soluble form. Fe concentration of this fraction in most samples amounts to almost one third of the total. Mn concentration of the sample from the Philippine Sea is high. This may be attributed to the manganese nodule or manganese rich sediment that is popular with the deep sea floor. Relatively much amount of Ba, Mg, Li, V, Zn, K, and Al dissolved in this fraction as well as Fe and Mn.

Among three groups, C(S) of Fe, Al and V is lower than C(F). Fe and Al concentrations in seawater are lower than that in river water as shown in Fig. 3. However, this fraction would be influenced by the redox conditions during sedimentation.

In this fraction, Mn, Ti, and V concentrations showed the positive correlation with Fe concentration as is shown in Fig. 4. These metals are thought to be fixed by co-precipitation with iron hydroxide. Adsorption capacity or binding strength depends on pH of pore water (Tessier *et al.*, 1985; Young and Harvey, 1992). Therefore, further development of adsorption modeling by iron hydroxide will need the data of pH.

H₂O₂ soluble fraction

H₂O₂ soluble fraction is thought to reflect organic matter complex and sulfide. Among the groups, the samples from the brackish-water lakes have the tendency that Fe, Mn concentrations were relatively high (C(B) > C(F), C(S)). They may be derived from iron sulfide. On the other hand, Ti, B, V, and Ca showed C(B) < C(F), C(S).

Silicate fraction

Silicate fraction is a major part for most elements, especially for Al, Ti, K, Sr, Ba, Li, and Rb. Each concentration of this fraction and group average are shown in Fig. 5. It reflects the origin of the sediment, geology of hinterland. therefore, sedimentary condition and diagenetic process may not influence so much on the silicate composition.

In Table 2, Na, Mg, Sr, Li and Mn showed a little difference among the groups. Sea sediments may be composed of much finer particles such as clay minerals, but any related trend was not observed in the silicate fraction.

3.2 Relationships among samples from fresh-water, brackish-water lakes, and sea

Table 3 is re-arranged from Table 2, showing clear relationships among three group averages. Shadows indicate that C(F) is < C(B), C(S) or C(B) is < C(S) at 98% confidence, and vertical dotted line shows that the ratio of metal concentration in seawater to in river water is 1.0. Between fresh-water lake samples and sea sam-

Table 3 Relationships among samples from fresh-water, brackish-water, and seawater in each fraction.

fraction	group	Fe	Al	Mn	Zn	Ti	Ba	V	Ca	Li	Sr	Rb	K	Mg	Na	group
1. Wash	fresh			>>				<<					<<		<<	seawater
2. AcONH ₄	fresh		>>	>>					<<	<<	<<		<<	<<	<<	seawater
3. AcOH	fresh												<<	<<	<<	seawater
4. NH ₂ OH	fresh	>>												<<		seawater
5. H ₂ O ₂	fresh															seawater
6. Silicate	fresh															seawater
0. Bulk	fresh															seawater
1. Wash	fresh		<<						<<		<<					brackish
2. AcONH ₄	fresh			>>			>>			<<				<<	<<	brackish
3. AcOH	fresh						>>							<<	<<	brackish
4. NH ₂ OH	fresh		>>			>>	>>	>>								brackish
5. H ₂ O ₂	fresh	<<	>>			>>	>>	>>	>>				<<			brackish
6. Silicate	fresh			>>						<<						brackish
0. Bulk	fresh							>>		<<					<<	brackish
1. Wash	brackish		>>				<<			>>	>>					seawater
2. AcONH ₄	brackish						<<						<<			seawater
3. AcOH	brackish						<<						<<			seawater
4. NH ₂ OH	brackish						<<									seawater
5. H ₂ O ₂	brackish	>>		>>		<<	<<		<<	>>					<<	seawater
6. Silicate	brackish			<<						>>	<<			<<	<<	seawater
0. Bulk	brackish						<<		<<	>>		>>				seawater

<< or >> : averages are not equal to each other at 98% confidence by t-test

ples, all elements that are $C(F) < C(S)$ are in right half area of dotted line, suggesting that the composition of interstitial water is one of the most important factors that control chemical composition of sediment. Between fresh-water and brackish-water lake samples, exceptions appeared for Fe, Al, V, and Ca. More exceptions are observed between brackish-water lake samples and sea samples. Ba and Li are typical exceptions, and the reason is not yet known. The probable reason may be the water chemistry such as ionic strength and sulfate concentration.

3.3 The ratios among fractions of diagenetic processes

A wash fraction is probably the component retained to the particles during sampling, and silicate fraction is also the background composition of the particles. Therefore, the authigenic minerals, diagenetic attached or sorbed elements are those of AcONH_4 soluble fraction, AcOH soluble fraction, $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction, and H_2O_2 soluble fraction. The ratios of each fraction in some elements are shown in Fig. 6.

The percentages of AcONH_4 soluble fraction of Na, Ca, Sr, Ba (except the samples from brackish-water), Mg, Mn (except the samples from seawater), K, Rb are relatively high. Ion exchange mechanism between clay mineral and groundwater reveals that alkaline metal ions and alkaline earth metal ions are easily exchangeable, and that Ca^{2+} is caught by the lattice and Na^+ is released into the water. This is well demonstrated in Fig. 7, where the amount of leached Na in this fraction showed a negative correlation with extracted Ca in the samples from fresh-water lakes and sea, respectively.

AcOH soluble fraction is important for Ca, Sr, Mg (samples from seawater), Mn (samples from seawater), Li and Zn, which chemically form insoluble carbonate precipitates such as CaCO_3 , SrCO_3 , MgCO_3 , MnCO_3 , Li_2CO_3 and ZnCO_3 . For these elements, the ratio of this fraction is usually more than 20%, sometimes exceed 50%. Deurer *et al.* (1978) studied carbonate associated metals from lacustrine sedi-

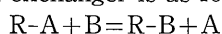
ments, and showed Mn and Zn were enriched in carbonate. Their results are consistent with this study.

$\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction is important in many elements because metal ions are scavenged by Fe and released with Fe. In particular, much amount of Ba, Mg, Mn, Li, V, Zn, and Al dissolve in this fraction. The important role played by iron hydroxides in the adsorption of trace metals in soils and sediments has been strongly emphasized (Young and Harvey, 1992; Lion *et al.*, 1982). In this fraction, Mn, Ti, and V correlated with Fe as was mentioned before. Probably they have been coprecipitated with iron hydroxide under oxidative condition, and released by the reducing reagent.

H_2O_2 soluble fraction ratio was high for Li, Zn, Al and Ti. This fraction may become important for the samples deposited under strongly reducing sedimentary condition and the organic complex forming elements. In this viewpoint, a further study will be needed.

3.4 Ion exchange and adsorption mechanism

From the empirical data, a simple model was examined. Ion exchange reaction between ion and exchanger is as follows.



In exchange equilibrium, $K_A^B = ([A]_s/[A]_r)/([B]_s/[B]_r)$ is constant where the square brackets represent concentrations and subscripts s and r represent solution and exchanger, respectively. On basis of hydrogen ion, the selectivity of the ion exchanger are shown to be

$$K_H^M = ([H]_s/[H]_r)/([M]_s/[M]_r)$$

$$[M]_r = K_H^M \cdot ([H]_r/[H]_s) \cdot [M]_s = K' \cdot [M]_s$$

and the order of K_H^M s is as follows.

$$\text{Li} \leq \text{Na} < \text{K}, \text{NH}_4 < \text{Rb} < \text{Cs}$$

$$\text{Mg} \leq \text{Ca} < \text{Sr} < \text{Ba}$$

This formula indicates that the concentration of metal ions adsorbed on the ion exchanger such as clay minerals is in proportion to solution concentration ($[M]_s$), and its coefficient (K') depends on pH and K_H^M . Although the empirical data obtained in this study cannot conduct the equilibrium constant directly, K' was calculated using AcONH_4 soluble fraction as $[M]_r$ and the elemental content in river water and seawater as $[M]_s$. The results are shown in Table 4 and

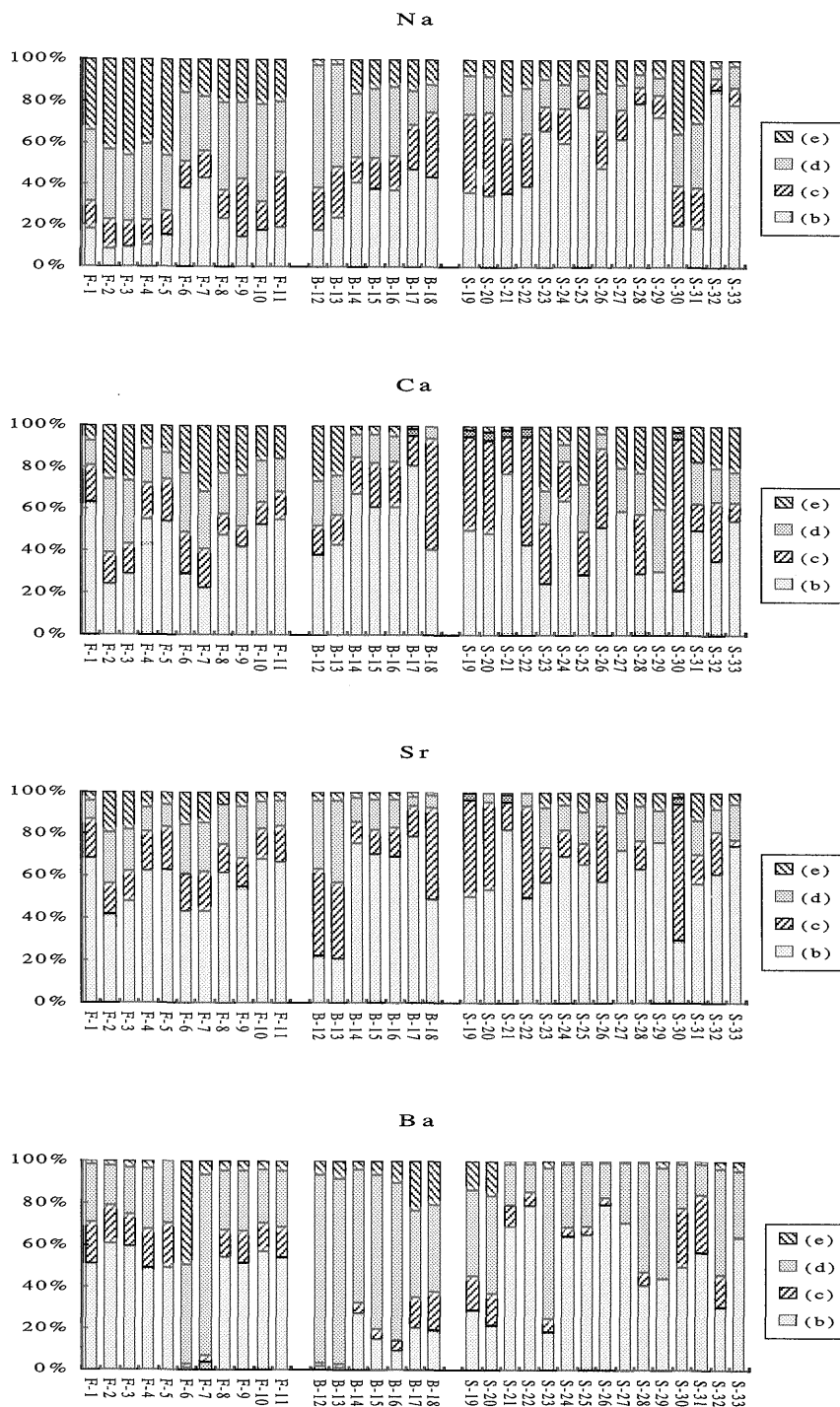


Fig. 6 Percentages among fractions of diagenetic processes. : (b) AcONH₄ soluble fraction ; (c) AcOH soluble fraction ; (d) NH₂OH · HCl soluble fraction ; (e) H₂O₂ soluble fraction. F-1 to F-11, B-12 to B-18 and S-19 to S-33 are fresh-water lake samples, brackish-water lake samples and sea samples, respectively.

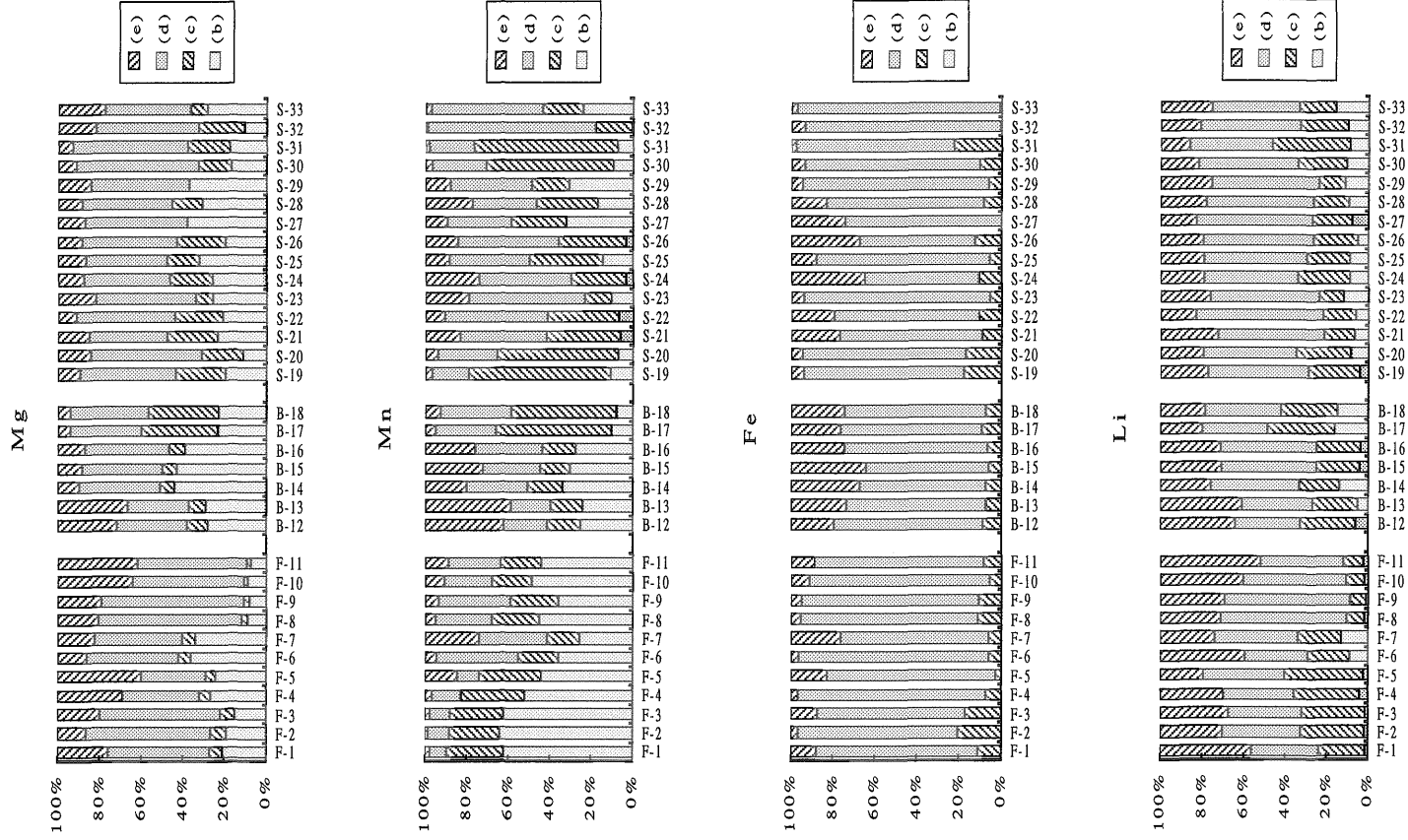


Fig. 6 (Continued)

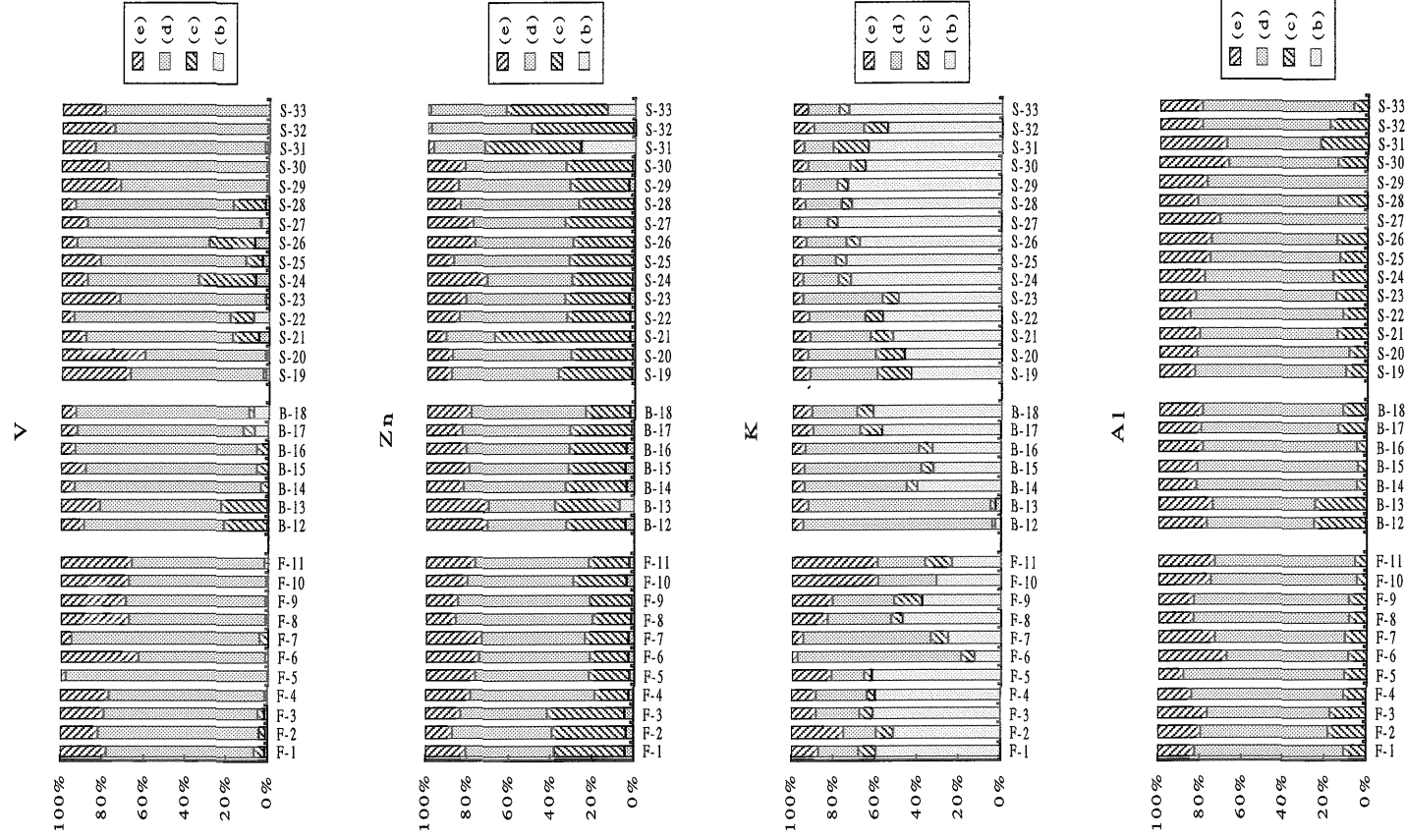


Fig. 6 (Continued)

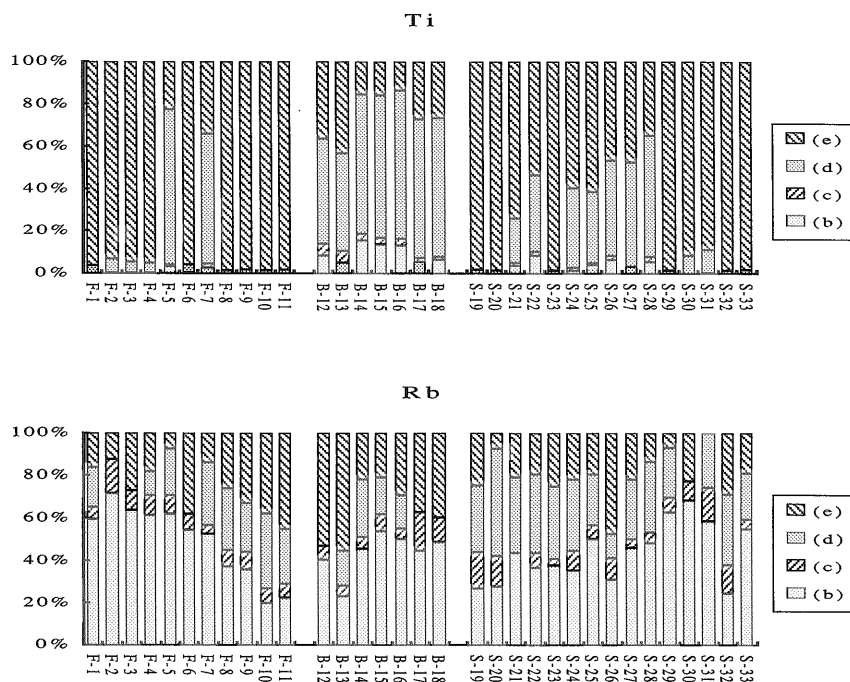


Fig. 6 (Continued)

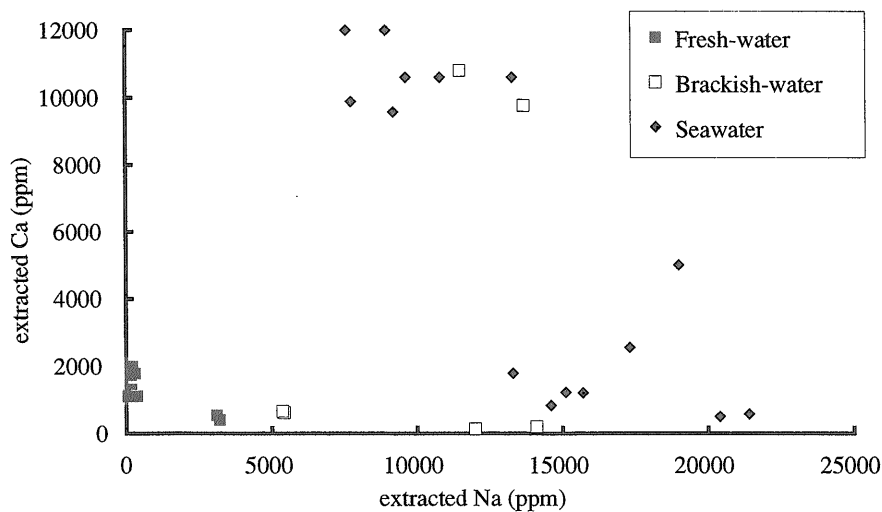


Fig. 7 Correlation between extracted Na and Ca in AcONH_4 soluble fraction.

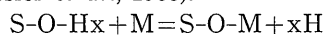
Table 4 Ion exchange constant (K') calculated from AcONH_4 soluble fraction. Elemental contents in river water and seawater were used for calculation. Elements in the parentheses are shown for reference.

log K'																			
element	Fe	Al	Mn	Zn	(Cu)	(Cr)	(Co)	Ti	Ba	(Ni)	V	(P)	Ca	Li	Sr	Rb	K	Mg	Na
lake sample	1.34	1.58	4.60	1.69	2.54	2.16	3.57	2.49	2.97	2.99	2.35	2.78	1.90	1.71	2.25	3.20	1.76	1.86	0.85
std	0.20	0.14	0.21	0.14	0.09	0.17	0.13	0.12	1.02	0.27	0.37	0.20	0.22	0.65	0.26	0.22	0.28	0.27	0.42
sea sample	3.52	3.50	5.72	3.63	3.85	2.61	3.64	2.82	3.55	3.06	2.25	2.36	0.92	0.62	0.67	1.01	0.34	-0.06	-1.30
std	0.45	0.33	0.56	0.76	0.25	0.26	0.47	0.13	0.70	0.32	0.47	0.19	0.52	0.33	0.22	0.20	0.33	0.21	0.50
std : standard deviation																			

std : standard deviation

Fig. 8. Although the fractional concentrations of Co, Ni, Cr, Cu and P might contain erroneous data, their results are also shown for reference. In Fig. 8, the elements are arranged in the order of seawater / river water concentration ratio. K' of Mn is the highest among the elements, suggesting that Mn is the strongest adsorbate and / or there may exist other mechanism. The variation of log K' for sea samples is larger than that for lake samples, and two lines cross each other. It suggests that K' and exchange capacity are lowered under the condition of high concentration environment. The K_H^M relationship, $\text{Na} < \text{K} < \text{Rb}$, $\text{Mg} \leq \text{Ca} < \text{Sr} < \text{Ba}$, is observed in general, though Li showed relatively high K' .

The adsorption behavior of metal ions on a hydroxide surface is also described as follows in a simplified model (Balistrieri and Murray, 1983; Tessier *et al.*, 1985).



$$*K_a = [\text{SOM}] \cdot [\text{H}^+]^x / ([\text{SOHx}] \cdot [\text{M}])$$

S-O-Hx and S-O-M represent surface site and surface complex, respectively, and $*K_a$ is an apparent average equilibrium constant. In the same manner,

$$[\text{SOM}] = *K_a \cdot [\text{SOHx}] \cdot [\text{M}] / [\text{H}^+]^x$$

indicates that adsorbed ion concentration is proportional to the metal content in water and depends on pH. Under relatively high pH condition such as sea, [SOM] would increase. However, $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction of the ele-

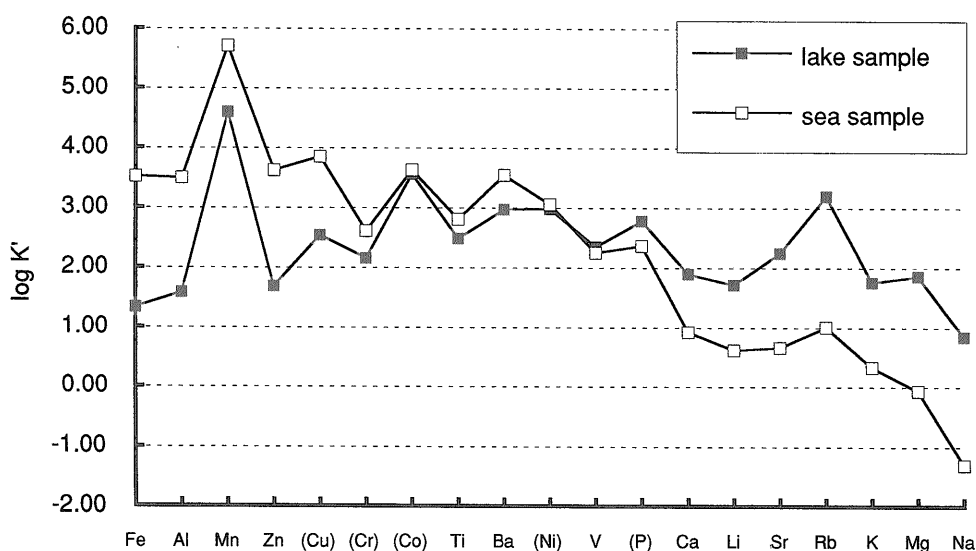


Fig. 8 Variation of ion exchange constant (K') calculated from AcONH_4 soluble fraction. Elements in the parentheses are shown for reference.

Table 5 Adsorption density (D) calculated from $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction. Elements in the parentheses are shown for reference.

	log D																	
	(Co)	(Ni)	Mn	(Cr)	(Cu)	Zn	Ti	V	Al	Ba	(P)	Rb	Li	Sr	K	Ca	Mg	Na
ave.C(F)	-3.92	-3.81	-2.18	-3.50	-3.52	-3.03	-3.01	-2.70	-0.10	-3.35	-1.35	-4.51	-2.95	-3.87	-2.11	-1.31	-0.92	-1.91
ave.C(B)	-3.96	-3.76	-1.99	-3.41	-3.42	-2.99	-3.35	-2.87	-0.21	-3.71	-1.65	-4.40	-2.58	-3.77	-1.22	-1.72	-0.71	-1.42
ave.C(S)	-3.56	-3.05	-1.90	-3.06	-2.92	-2.55	-2.99	-2.73	0.00	-2.86	-1.31	-4.20	-2.42	-3.38	-1.34	-0.91	-0.24	-1.41
average	-3.77	-3.46	-2.01	-3.28	-3.23	-2.81	-3.08	-2.75	-0.07	-3.20	-1.40	-4.33	-2.63	-3.63	-1.57	-1.22	-0.57	-1.58
std	0.34	0.45	0.39	0.30	0.35	0.35	0.31	0.16	0.20	0.58	0.22	0.26	0.41	0.38	0.54	0.52	0.41	0.39

$D = [M] / [Fe]$; [] is molar concentration of $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction .

ment abundant in river water didn't show such trend as $C(S) > C(F)$ except Ba.

Tessier *et al.* (1985) introduced the adsorption density (D in this study, though they used Γ) calculated by $[\text{SOM}] / [\text{Fe}]_{\text{total}}$, i.e., metal / Fe molar ratio obtained by 0.04M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% AcOH at 96°C for 6 hrs. The adsorption density calculated from this study is shown in Table 5 and Fig. 9. Tessier *et al.* (1985) studied the adsorption densities of Zn, Pb, Cu, Cd and Ni in lake sediments. Logarithm of D of Zn ranged from -1.9 to -3.8, that of Cu ranged from -2.6 to -2.9, and that of Ni ranged from -2.3 to -3.5. In this study, the average of log D

(Zn) in lake sediment was -3.03 and -2.99, and overall average was -2.81. The average of log D for Cu and Ni was -3.23 and -3.46, respectively. They are in rough accord with the result by Tessier *et al.* (1985), though the leaching condition employed in this study is a little different. In Fig. 9, the elemental data are arranged in the order of seawater concentration, and log D shows a gradually increasing trend. Mn and Al showed extraordinary high values, suggesting that they adsorb strongly to oxyhydroxide and / or the other adsorption mechanism may exist.

For a given pH, one can define equilibrium

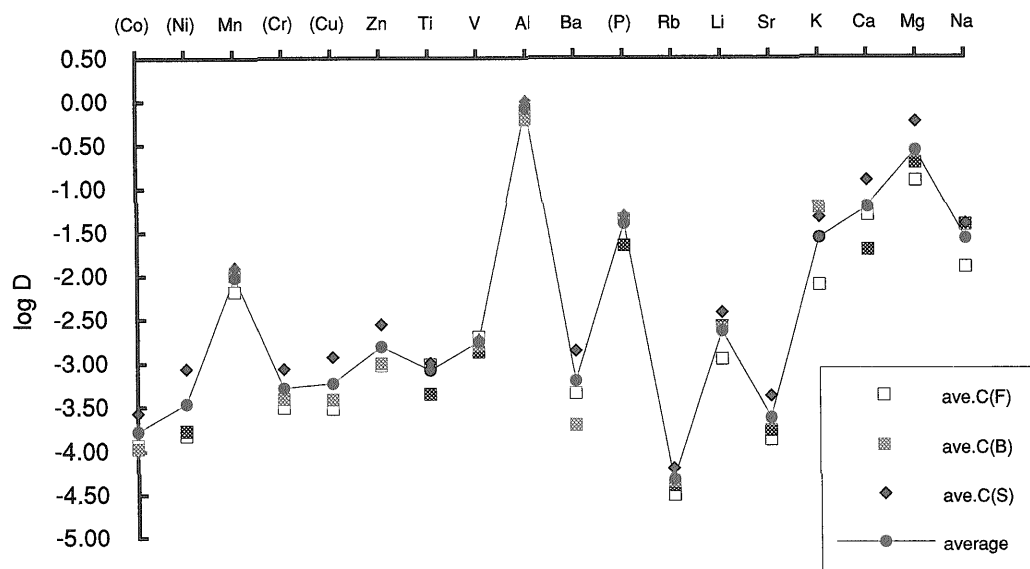


Fig. 9 Variation of adsorption density (D). Elements are arranged in the order of seawater content. F, B and S indicate fresh-water lake sample, brackish-water lake sample and sea sample, respectively. Elements in the parentheses are shown for reference.

Table 6 Equilibrium constant (K) calculated from $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction. Elements for the parentheses are shown for reference.

	log K																	
	(Co)	(Ni)	Mn	(Cr)	(Cu)	Zn	Ti	V	Al	Ba	(P)	Rb	Li	Sr	K	Ca	Mg	Na
Lake sample	4.85	4.48	4.72	4.21	3.44	3.49	4.19	5.05	4.73	3.49	4.84	3.42	3.41	2.22	2.12	2.11	2.85	1.65
Sea sample	5.73	5.02	7.14	5.35	5.58	5.78	4.69	4.67	7.13	4.13	4.48	1.65	2.16	0.66	0.64	1.07	1.03	-1.09

constant K, assuming that $[\text{SOHx}] = [\text{SOHx}]_{\text{total}} = n \cdot [\text{Fe}]_{\text{total}}$, where n represents the number of binding sites per iron oxyhydroxide.

$$K = n \cdot K_a / [\text{H}]^x = D / [\text{M}], \text{ where } D = [\text{SOM}] / [\text{Fe}]_{\text{total}}$$

K values for fresh-water lake samples and sea-water samples are calculated using river water concentration and seawater concentration, respectively. The results are listed in Table 6 and Fig. 10. One can point out three remarkable characteristics between two lines of Fig. 10. The first point is that the variation of log K of various elements calculated from lake samples is smaller than that from sea samples. The second is that log K of Mn and Al from sea samples is >7 , higher than any other elements, though that from lake sample is nearly equal to that of the transition metal element. The third

is that log K changes dramatically; for sea samples, that of the transition metal (Co-V) ranges from 4.7 to 7.1, and that of Rb-Mg ranges from 0.6 to 2.2. This suggests that the transition metal elements are easily adsorbed by iron hydroxide and Na is the least adsorbed element. And Al and Mn may be controlled by strong adsorption mechanism in sea environment.

4. Conclusion

The selective chemical leaching method was applied to recent surface sediments from fresh-water lakes, brackish-water lakes in Japan and sea around Japan. Chemical composition of each fraction was determined and relationships among samples and elements were examined.

The majority of Na dissolved in the water-

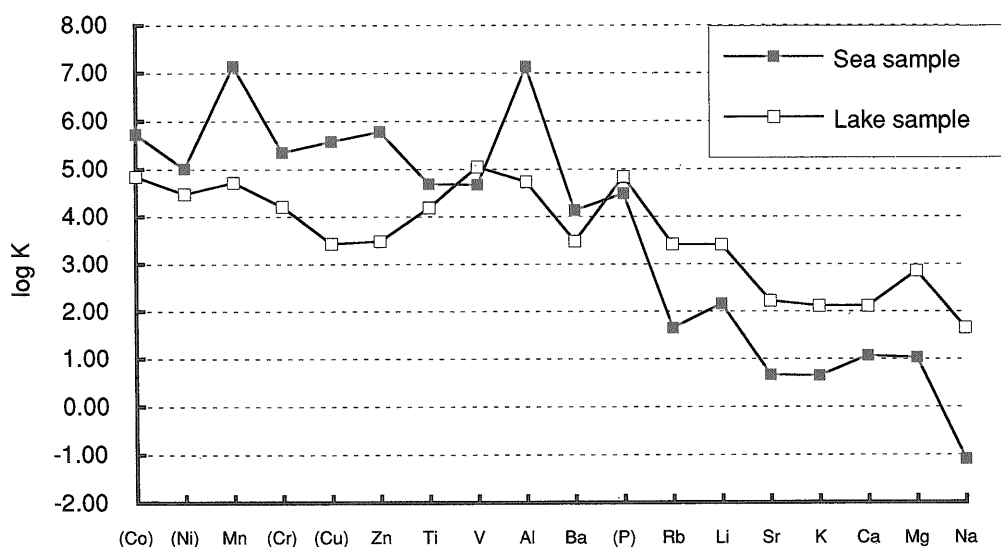


Fig. 10 Variations of equilibrium constant (K) calculated from sea samples and lake samples. Elements in the parentheses are shown for reference.

soluble fraction. Most elements studied in this study showed the tendency of $C(B), C(S) > C(F)$ except for Mn, Rb and Ba, where $C(B), C(S)$ and $C(F)$ are average concentrations of samples from brackish-water lakes, from sea, from fresh-water lakes, respectively. AcONH_4 soluble fraction of Fe, Mn, Al and Ba showed $C(F) > C(B), C(S)$. This may be ascribed to the original water composition around the sediments. AcOH soluble fraction is important for carbonate forming elements, and Fe showed the trend of $C(F) > C(S)$ as expected from seawater / river water ratio. $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble fraction is mainly composed of Fe, and many metal ions dissolved.

The relationship among $C(F), C(B)$ and $C(S)$ was shown to depend mainly on the seawater / river water ratios and each chemical condition. It also depends on mineral type, degrees of weathering and alteration, grain size, surface form, and surface coating matrix. Many case studies will be desired to testify the relationship.

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日本における淡水湖、汽水湖及び日本周辺海域の
堆積物の選択的分別化学溶解法による研究

金井 豊

要 旨

選択的分別化学溶解法を淡水湖、汽水湖及び日本周辺海域の表層堆積物に適用した。それぞれのフラクションの化学組成を調べ、試料間や元素間の関係を調べた。

洗浄フラクションには多くの Na が溶出した。本研究で調べた元素の中で Mn, Rb, Ba を除く多くの元素について、淡水湖試料の溶出量は汽水湖や海域試料よりも少なかった。酢酸アンモニウム可溶フラクションでは Fe, Al, Mn 濃度が淡水湖試料で高かった。これは堆積物のおかれた環境の水質によるものと考えられる。酢酸可溶フラクションは炭酸塩を作る元素にとって重要であり、海水／河川水濃度比から推測されるように Fe の淡水湖試料からの溶出量は海域試料よりも高かった。塩酸ヒドロキシルアミン可溶フラクションは主として Fe からなり、多くの金属イオンを伴っていた。

淡水湖試料、汽水湖試料及び海域試料のそれぞれの溶出量の関係は、主として海水／河川水濃度比と化学的狀態によっていることが示された。それはさらに鉱物の種類、風化変質の度合い、粒度、表面形態や被覆マトリックスにもよっている。これらを詳細に実証するためには、より多くのケーススタディが必要である。

Appendix table Elemental concentrations of each fractions (1g sample) : (a) wash fraction ; (b) AcONH₄ soluble fraction ; (c) AcOH soluble fraction ; (d) NH₄OH · HCl soluble fraction ; (e) H₂O₂ soluble fraction ; (f) silicate fraction ; (g) bulk composition.

Element	Ti							Al							Fe						
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
Sample	ppm	ppm	ppm	ppm	ppm	%	%	ppm	ppm	%	%	%	%	%	ppm	ppm	%	%	%	%	%
F-1	1	1	1	19	489	0.16	0.20	100	13	0.13	0.85	0.21	4.58	5.82	95	11	0.16	1.09	0.17	1.46	2.86
F-2	0	1	1	15	226	0.31	0.32	31	15	0.21	0.69	0.23	7.60	8.72	26	12	0.26	0.95	0.04	3.75	4.95
F-3	2	1	1	16	295	0.29	0.32	102	11	0.22	0.77	0.31	7.48	8.86	64	8	0.27	1.11	0.20	3.02	4.63
F-4	1	1	0	15	303	0.39	0.40	49	26	0.17	1.17	0.26	8.26	10.00	32	17	0.15	1.79	0.06	3.33	5.09
F-5	1	1	0	19	6	0.32	0.42	47	13	0.17	1.24	0.20	7.11	10.80	34	12	0.09	2.23	0.49	3.11	5.71
F-6	1	1	0	16	396	0.40	0.33	122	27	0.08	0.54	0.30	8.66	8.50	119	24	0.13	1.92	0.08	3.52	5.80
F-7	0	1	0	16	9	0.20	0.32	85	13	0.08	0.49	0.21	6.95	7.92	83	8	0.14	1.61	0.54	2.63	4.94
F-8	1	1	0	10	677	0.40	0.43	22	13	0.06	0.50	0.11	7.29	7.95	33	16	0.28	2.12	0.12	2.51	4.76
F-9	2	1	0	13	799	0.45	0.47	22	10	0.06	0.56	0.13	7.72	8.66	34	13	0.30	2.39	0.15	2.47	5.05
F-10	0	1	0	10	713	0.22	0.60	104	20	0.03	0.49	0.17	8.74	9.64	276	29	0.16	2.44	0.26	4.87	7.54
F-11	0	1	0	12	717	0.38	0.52	105	15	0.04	0.48	0.19	7.94	8.66	293	26	0.23	2.23	0.31	4.03	6.56
B-12	0	1	1	7	5	0.34	0.31	1220	48	0.20	0.41	0.19	7.61	8.93	250	26	0.25	2.01	0.59	1.75	4.72
B-13	0	1	1	7	7	0.32	0.27	801	23	0.18	0.37	0.20	6.99	7.98	269	16	0.20	1.80	0.72	1.48	3.98
B-14	0	1	0	3	1	0.41	0.37	37	13	0.03	0.44	0.11	8.62	9.14	54	7	0.19	1.58	0.87	2.62	5.20
B-15	0	1	0	3	1	0.42	0.37	47	10	0.02	0.41	0.10	8.49	9.09	90	5	0.16	1.59	0.98	2.38	4.92
B-16	0	1	0	4	1	0.42	0.37	69	14	0.02	0.42	0.12	8.36	8.96	87	8	0.17	1.69	0.64	2.40	4.74
B-17	0	1	0	9	4	0.37	0.34	64	37	0.08	0.44	0.14	11.10	11.70	14	11	0.11	0.79	0.29	2.61	3.76
B-18	0	1	0	9	4	0.35	0.33	46	58	0.06	0.38	0.12	10.40	11.00	12	13	0.08	0.73	0.28	2.56	3.64
S-19	0	1	0	8	411	0.41	0.39	15	10	0.05	0.34	0.08	7.41	7.47	16	9	0.26	1.08	0.09	3.09	4.26
S-20	0	1	0	6	493	0.46	0.44	19	12	0.05	0.42	0.10	7.82	8.28	18	13	0.30	1.38	0.10	3.90	5.46
S-21	0	1	0	3	10	0.30	0.28	25	4	0.07	0.33	0.10	7.04	7.17	12	2	0.09	0.61	0.21	2.08	2.86
S-22	1	1	0	4	5	0.34	0.32	47	16	0.06	0.37	0.08	7.23	7.70	29	16	0.11	0.71	0.21	2.48	3.52
S-23	1	1	0	9	687	0.26	0.31	51	9	0.11	0.49	0.13	5.47	5.98	45	12	0.08	1.25	0.08	1.87	3.23
S-24	2	1	0	11	18	0.30	0.28	41	6	0.12	0.45	0.16	5.29	5.90	21	4	0.13	0.65	0.42	2.08	3.20
S-25	3	1	0	5	9	0.37	0.36	69	6	0.13	0.61	0.25	6.90	7.43	54	10	0.06	0.90	0.13	3.92	4.44
S-26	2	1	0	8	8	0.34	0.32	38	12	0.08	0.33	0.14	6.39	6.61	20	12	0.10	0.43	0.26	2.53	3.09
S-27	2	1	0	7	7	0.31	0.28	42	4	0.00	0.40	0.17	5.64	5.90	36	4	0.00	0.57	0.20	2.51	3.19
S-28	1	1	0	7	4	0.38	0.35	42	9	0.12	0.58	0.16	7.05	7.85	32	9	0.09	0.85	0.19	3.06	4.00
S-29	1	1	0	6	368	0.26	0.29	35	7	0.00	0.46	0.14	6.04	6.48	35	13	0.06	0.82	0.05	2.66	3.50
S-30	0	0	0	37	417	0.32	0.66	17	2	0.08	0.32	0.20	6.92	6.90	24	4	0.12	1.03	0.08	6.29	7.15
S-31	2	1	1	27	228	0.44	0.44	53	14	0.34	0.66	0.47	8.07	9.39	85	29	0.37	1.23	0.04	0.50	6.44
S-32	1	0	0	7	481	0.41	0.36	173	5	0.13	0.43	0.14	8.80	8.66	53	6	0.01	1.25	0.09	3.54	4.71
S-33	1	1	0	9	486	0.49	0.50	40	1	0.09	0.97	0.28	9.01	9.60	54	0	0.03	2.57	0.08	6.38	8.66
average(X) and standard deviation(σ)																					
Element	Ti							Al							Fe						
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
Sample	ppm	ppm	ppm	ppm	ppm	%	%	ppm	ppm	%	%	%	%	%	ppm	ppm	%	%	%	%	%
X(F)	1	1	0	15	421	0.32	0.39	72	16	0.11	0.71	0.21	7.48	8.68	99	16	0.20	1.81	0.22	3.15	5.26
σ (F)	1	0	0	3	282	0.09	0.11	38	6	0.07	0.28	0.06	1.13	1.29	97	7	0.07	0.55	0.17	0.91	1.19
X(B)	0	1	0	6	3	0.38	0.34	326	29	0.09	0.41	0.14	8.80	9.54	111	12	0.17	1.46	0.62	2.26	4.42
σ (B)	0	0	0	3	2	0.04	0.04	483	19	0.08	0.03	0.04	1.46	1.31	106	7	0.06	0.50	0.27	0.46	0.62
X(S)	1	1	0	10	242	0.36	0.37	47	8	0.09	0.48	0.17	7.01	7.42	36	9	0.12	1.02	0.15	3.13	4.51
σ (S)	1	0	0	9	244	0.07	0.10	38	4	0.08	0.17	0.10	1.13	1.19	20	7	0.11	0.52	0.10	1.56	1.71
X(T)	1	1	0	11	251	0.35	0.37	115	15	0.10	0.54	0.18	7.54	8.29	73	12	0.16	1.38	0.27	2.95	4.74
σ (T)	1	0	0	7	273	0.08	0.10	240	12	0.07	0.23	0.08	1.35	1.49	80	8	0.09	0.62	0.25	1.22	1.39

Appendix table (Continued)

Mg							Ca							Mn						
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
%	%	%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	%
0.01	0.03	0.01	0.06	0.03	0.32	0.47	0.06	0.20	0.06	0.04	0.02	0.38	0.75	143	395	173	50	16	212	0.10
0.00	0.02	0.01	0.06	0.01	1.38	1.47	0.03	0.13	0.08	0.19	0.14	2.83	3.32	121	535	204	84	14	754	0.17
0.01	0.03	0.01	0.10	0.04	1.06	1.22	0.03	0.18	0.09	0.18	0.16	2.15	2.72	123	548	222	87	21	592	0.16
0.01	0.02	0.00	0.03	0.03	0.86	0.96	0.12	0.18	0.06	0.05	0.04	0.67	1.07	246	366	215	100	23	374	0.13
0.01	0.02	0.01	0.03	0.04	0.80	1.02	0.09	0.20	0.08	0.05	0.05	1.26	1.11	204	415	281	98	145	411	0.14
0.26	0.09	0.02	0.11	0.04	0.95	1.44	0.16	0.06	0.04	0.05	0.04	0.73	1.70	633	177	98	193	29	394	0.17
0.23	0.10	0.02	0.13	0.05	0.72	1.27	0.10	0.04	0.04	0.05	0.06	1.23	1.48	342	123	76	156	126	366	0.12
0.01	0.03	0.01	0.20	0.06	0.73	1.03	0.02	0.11	0.03	0.05	0.06	0.41	0.68	47	265	133	158	32	331	0.10
0.01	0.03	0.01	0.24	0.07	0.81	1.15	0.02	0.11	0.03	0.07	0.06	0.37	0.66	40	210	134	202	38	314	0.09
0.01	0.02	0.00	0.11	0.08	1.52	1.72	0.07	0.11	0.02	0.04	0.04	0.41	0.70	172	216	84	101	41	555	0.12
0.01	0.02	0.00	0.11	0.08	1.20	1.44	0.06	0.11	0.03	0.03	0.03	0.33	0.58	140	185	83	106	47	482	0.10
0.33	0.04	0.01	0.04	0.04	0.43	0.90	0.16	0.02	0.01	0.01	0.01	0.16	0.33	399	44	29	37	67	216	0.08
0.36	0.04	0.01	0.04	0.05	0.40	0.90	0.17	0.02	0.01	0.01	0.01	0.17	0.36	352	45	28	36	77	213	0.07
0.16	0.16	0.03	0.14	0.04	0.74	1.30	0.07	0.06	0.02	0.01	0.00	0.21	0.37	228	187	92	160	111	174	0.10
0.20	0.16	0.03	0.14	0.04	0.74	1.30	0.09	0.06	0.02	0.01	0.00	0.21	0.39	301	185	86	167	170	171	0.11
0.24	0.16	0.03	0.16	0.05	0.74	1.37	0.10	0.07	0.02	0.01	0.01	0.20	0.40	377	203	120	238	179	169	0.13
0.08	0.16	0.25	0.23	0.04	0.73	1.49	0.18	0.98	0.18	0.04	0.02	0.66	1.88	10	130	718	372	65	330	0.16
0.07	0.14	0.21	0.22	0.04	0.75	1.46	0.17	1.08	1.43	0.14	0.02	0.82	2.47	6	72	460	308	69	342	0.13
0.08	0.13	0.16	0.31	0.07	0.91	1.60	0.13	1.06	0.96	0.07	0.04	0.39	2.54	6	73	458	119	23	306	0.09
0.07	0.13	0.24	0.64	0.19	1.58	2.85	0.13	1.06	0.98	0.09	0.06	1.08	3.35	2	29	236	114	25	419	0.08
0.04	0.08	0.09	0.13	0.05	0.73	1.10	0.12	1.20	0.27	0.05	0.03	0.29	4.11	0	8	47	55	22	222	0.04
0.03	0.07	0.08	0.16	0.03	0.83	1.22	0.09	1.20	1.47	0.11	0.03	0.51	3.40	1	11	50	73	14	313	0.05
0.29	0.11	0.04	0.20	0.08	0.79	1.52	0.23	0.06	0.07	0.04	0.07	0.72	1.08	32	9	12	50	19	258	0.04
0.10	0.15	0.12	0.24	0.07	0.73	1.40	0.19	0.50	0.15	0.06	0.07	0.92	1.83	1	4	34	56	33	285	0.04
0.08	0.21	0.10	0.26	0.09	1.00	1.72	0.05	0.12	0.09	0.10	0.12	1.01	1.42	5	32	79	86	26	421	0.07
0.03	0.07	0.08	0.15	0.04	0.95	1.24	0.09	0.99	0.74	0.13	0.07	1.53	3.46	0	3	27	40	13	477	0.05
0.09	0.13	0.00	0.16	0.04	0.70	1.13	0.14	0.26	0.00	0.09	0.09	1.40	1.94	5	60	50	57	20	435	0.06
0.08	0.17	0.08	0.23	0.06	0.97	1.58	0.03	0.09	0.08	0.06	0.06	0.91	1.19	16	40	72	74	55	358	0.06
0.23	0.13	0.00	0.17	0.06	0.82	1.40	0.10	0.05	0.00	0.05	0.07	1.17	1.42	95	49	28	63	19	407	0.07
0.09	0.09	0.08	0.30	0.04	1.64	2.11	0.18	1.06	3.56	0.16	0.14	4.26	8.79	4	60	402	170	21	1120	0.17
0.05	0.07	0.08	0.23	0.03	1.82	2.20	0.13	0.96	0.25	0.39	0.33	4.96	6.96	4	37	353	109	9	1150	0.17
0.00	0.05	0.09	0.21	0.08	1.14	1.50	0.00	0.12	0.10	0.06	0.07	0.44	1.04	3	20	571	2600	38	389	0.34
0.04	0.29	0.08	0.41	0.23	1.75	2.66	0.03	0.18	0.03	0.05	0.07	0.56	0.93	100	496	400	1100	61	414	0.26

Mg							Ca							Mn						
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
%	%	%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	%
0.05	0.04	0.01	0.11	0.05	0.94	1.20	0.07	0.13	0.05	0.07	0.06	0.98	1.34	201	312	155	121	48	435	0.13
0.10	0.03	0.00	0.06	0.02	0.34	0.33	0.05	0.05	0.02	0.06	0.04	0.83	0.91	167	148	69	49	45	151	0.03
0.20	0.12	0.08	0.14	0.04	0.65	1.25	0.13	0.33	0.24	0.03	0.01	0.35	0.89	239	124	219	188	105	231	0.11
0.11	0.06	0.10	0.08	0.01	0.16	0.25	0.04	0.48	0.53	0.05	0.01	0.27	0.90	167	70	266	128	50	75	0.03
0.09	0.13	0.09	0.25	0.08	1.09	1.68	0.11	0.59	0.58	0.10	0.09	1.34	2.90	18	62	188	318	27	465	0.11
0.08	0.06	0.06	0.13	0.06	0.40	0.54	0.06	0.48	0.94	0.09	0.07	1.38	2.29	33	122	194	685	15	281	0.09
0.10	0.09	0.06	0.18	0.06	0.95	1.43	0.10	0.38	0.33	0.08	0.06	1.01	1.95	126	159	183	225	50	405	0.11
0.11	0.07	0.07	0.12	0.04	0.37	0.48	0.06	0.43	0.71	0.07	0.06	1.10	1.87	157	164	178	466	46	227	0.06

Appendix table (Continued)

Element	Na							K							Zn						
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
Sample	%	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
F-1	0.02	37	28	71	70	0.39	0.54	126	152	21	48	34	0.43	0.55	0	1	9	11	5	26	51
F-2	0.02	47	77	185	236	1.49	1.68	135	133	21	40	65	0.96	1.14	0	1	8	11	3	40	66
F-3	0.02	46	61	160	227	1.27	1.36	49	171	19	57	34	0.88	0.99	1	1	10	11	5	38	84
F-4	0.03	22	25	79	86	0.75	0.95	448	160	10	65	32	0.95	1.06	0	1	5	18	7	72	109
F-5	0.02	41	31	71	123	1.23	0.91	174	193	11	48	60	1.23	1.14	0	1	7	18	8	45	114
F-6	0.31	257	85	221	107	0.77	1.74	179	182	94	1130	40	0.96	1.59	10	1	6	18	9	73	99
F-7	0.32	292	85	175	121	1.30	1.91	139	381	121	918	87	1.30	1.66	9	1	7	17	10	42	92
F-8	0.01	27	17	50	24	1.15	1.28	111	142	17	90	53	2.03	2.32	0	1	10	35	8	54	112
F-9	0.01	19	38	49	27	1.17	1.27	122	117	42	90	61	2.22	2.49	0	1	13	40	10	53	126
F-10	0.04	18	15	48	22	0.64	0.78	109	43	0	38	58	1.56	1.76	2	2	13	25	10	101	155
F-11	0.02	25	35	44	26	0.56	0.65	53	39	21	38	68	1.46	1.60	2	1	9	26	11	90	144
B-12	1.20	421	488	1380	67	0.58	2.43	102	46	23	1400	92	1.51	1.98	31	1	6	8	6	51	110
B-13	1.41	453	478	930	49	0.64	2.49	0	47	42	1490	140	1.47	1.92	36	2	9	9	9	48	110
B-14	0.54	166	51	123	66	0.82	1.62	443	476	61	586	72	1.69	2.11	8	2	14	23	9	48	112
B-15	0.54	147	57	127	55	0.83	1.50	495	385	71	665	75	1.72	2.10	13	2	14	24	10	46	110
B-16	0.54	132	59	118	47	0.88	1.56	459	398	76	658	83	1.74	2.16	14	2	15	26	10	45	114
B-17	1.37	262	120	89	83	1.32	2.92	934	525	94	207	96	1.47	1.87	1	0	10	17	6	55	93
B-18	1.15	303	216	91	85	1.35	2.91	870	517	65	182	78	1.43	1.74	0	1	6	17	7	54	91
S-19	0.96	174	179	90	36	1.20	2.31	487	240	88	178	47	1.97	2.19	0	1	16	24	6	55	108
S-20	1.08	168	200	84	40	1.16	2.31	636	309	92	212	49	1.73	1.99	0	1	15	29	6	61	117
S-21	0.89	133	97	78	62	1.21	2.22	781	563	117	313	92	2.12	2.42	1	5	124	45	18	39	241
S-22	0.76	166	109	94	58	1.40	2.28	607	616	98	290	85	2.16	2.56	0	1	13	22	7	39	88
S-23	2.14	634	113	128	88	1.14	3.72	914	970	157	734	106	1.17	1.60	7	1	13	21	8	33	88
S-24	1.90	719	199	139	139	1.19	3.30	1090	1320	118	304	96	1.08	1.44	1	1	20	28	20	32	108
S-25	1.57	1790	193	162	177	1.56	3.19	1030	2360	165	508	150	1.61	2.05	0	0	20	35	8	52	118
S-26	0.78	311	120	116	105	1.59	2.43	695	860	78	242	84	1.51	1.78	0	0	10	17	8	35	73
S-27	1.73	846	197	161	165	1.52	3.24	914	1320	78	222	59	1.11	1.31	0	0	15	21	11	43	93
S-28	1.46	1800	174	147	156	1.32	2.95	934	2170	148	530	184	1.65	2.07	0	0	13	28	8	47	103
S-29	2.04	1060	155	121	127	1.28	3.51	1390	1480	102	356	80	1.31	1.66	3	1	11	20	6	46	91
S-30	1.33	161	156	201	283	1.77	3.10	671	408	48	125	47	0.57	0.69	0	0	8	13	5	61	99
S-31	0.92	258	275	426	417	1.91	2.89	521	408	106	88	32	0.53	0.66	0	12	20	11	1	110	102
S-32	1.51	3060	210	170	125	1.71	3.30	231	1300	276	562	240	2.54	2.78	0	2	91	88	4	298	273
S-33	1.33	3620	404	456	143	0.87	2.48	498	2830	191	562	279	1.54	1.89	42	200	707	528	24	134	1760

average(X) and standard deviation(σ)

Element	Na							K							Zn						
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
Sample	%	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
X(F)	0.07	76	45	105	97	0.97	1.19	150	156	34	233	54	1.27	1.48	2	1	9	21	8	58	105
σ (F)	0.12	99	27	66	77	0.36	0.46	107	90	38	394	17	0.53	0.58	4	0	2	10	3	23	31
X(B)	0.96	269	210	408	65	0.92	2.20	472	342	62	741	91	1.58	1.98	15	1	10	18	8	49	106
σ (B)	0.41	131	195	527	15	0.30	0.63	350	209	23	521	23	0.13	0.15	14	1	4	7	2	4	9
X(S)	1.36	993	185	171	141	1.39	2.88	760	1144	124	348	109	1.51	1.81	4	15	73	62	9	72	231
σ (S)	0.46	1107	77	115	99	0.28	0.50	291	797	57	189	73	0.57	0.61	11	51	178	130	6	69	427
X(T)	0.85	534	144	199	110	1.15	2.17	495	644	81	393	87	1.44	1.74	6	7	38	39	9	63	162
σ (T)	0.68	854	123	269	85	0.38	0.91	371	713	61	389	56	0.50	0.56	11	35	122	89	5	48	290

Appendix table (Continued)

Y											
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
2	1	3	41	13	35	95	5	22	6	3	1
1	0	1	20	5	84	118	2	16	5	9	7
0	0	1	27	8	80	124	3	21	6	9	8
0	1	0	58	18	90	173	8	26	8	5	3
0	0	0	61	1	65	183	7	27	9	5	3
0	0	0	1	29	17	96	106	15	11	5	6
0	0	0	24	1	48	88	11	9	4	5	3
0	0	0	0	19	9	69	104	1	7	1	2
0	0	0	24	11	79	121	1	6	1	3	1
1	0	0	34	17	60	159	2	7	2	1	1
0	0	0	0	0	0	0	2	7	2	1	1
0	0	0	1	31	17	66	138	15	4	6	5
1	0	5	16	3	47	79	13	74	68	5	1
2	0	0	14	7	79	106	12	68	54	5	1
0	0	0	15	11	89	129	8	62	10	3	1
3	1	1	8	1	57	81	6	61	54	7	1
3	1	1	8	1	63	90	17	14	4	5	2
0	0	0	23	9	56	100	15	32	6	5	3
5	1	6	11	3	53	87	17	14	4	5	2
4	1	2	16	4	93	135	7	27	4	6	4
4	1	3	10	1	59	89	5	37	17	8	3
3	0	0	17	2	83	90	13	25	0	6	3
2	0	3	10	2	83	123	5	21	4	5	2
0	0	0	18	7	61	104	8	23	0	5	3
2	0	0	18	5	119	274	14	57	125	6	4
1	0	0	25	5	182	249	11	56	13	16	13
6	0	0	19	6	79	127	0	23	7	4	3
0	0	0	0	0	19	127	5	47	2	11	3

Sr											
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
27	52	20	28	2	132	235	42	78	1	3	1
20	34	10	17	1	254	314	7	208	236	5	9
34	10	17	1	3	238	326	8	172	214	5	9
31	67	26	39	5	220	498	3	152	193	5	8
81	68	29	40	0	290	387	3	113	200	5	9
63	0	0	6	6	226	323	4	155	162	5	6
0	0	0	0	0	0	0	3	122	154	5	4
0	0	0	0	0	0	0	1	67	82	1	2
1	46	11	24	4	4	4	1	67	82	1	3
1	44	13	24	4	416	535	1	67	82	1	3
1	80	19	35	6	324	518	1	43	61	1	1
1	68	18	33	6	287	436	1	38	53	0	3
0	0	0	0	0	0	0	1	36	71	5	1
0	0	0	0	0	0	0	1	69	228	5	1
0	1	1	2	1	285	359	1	64	249	3	1
0	97	15	27	2	269	496	1	73	230	7	1
0	67	5	11	5	311	515	2	77	143	5	2
1	20	7	76	4	198	389	3	85	172	5	3
1	128	9	59	9	191	464	3	85	172	5	3
1	297	19	134	8	288	819	4	100	172	6	4
1	99	4	21	1	250	487	3	133	243	8	3
2	218	0	86	3	202	589	3	101	175	6	3
2	218	0	86	3	202	589	5	21	4	5	2
1	86	13	108	2	276	565	8	23	0	5	3
1	131	0	157	10	212	618	14	57	125	6	4
0	46	26	19	1	86	205	11	56	13	16	13
1	84	40	21	2	95	270	0	23	7	4	3
0	49	24	79	6	308	603	3	85	154	4	3
0	72	0	35	5	112	269	3	70	158	4	3

Ba											
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
20	46	14	24	3	278	401	14	22	2	79	100
1	0	1	14	6	18	32	1	0	1	14	6
1	0	2	18	2	61	89	1	0	2	18	2
2	0	2	5	1	18	23	2	0	2	5	1
2	0	2	13	4	34	61	2	0	2	13	4
2	0	2	12	49	3	79	161	0	0	1	23
2	0	0	10	35	3	246	412	0	0	1	23
1	0	0	2	39	2	72	137	0	0	0	1

Appendix table (Continued)

Element	Li							Rb							P	Co	Ni	Cr	Cu	Cs
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
F-1	0	0	0	1	1	10	13	0	2	0	1	0	24	41	672	0	27	31	27	11
F-2	0	0	0	0	0	12	13	2	1	0	0	0	43	39	521	14	1	27	19	17
F-3	0	0	0	1	0	12	14	0	2	0	0	1	36	41	657	15	25	25	26	13
F-4	1	1	4	4	4	48	68	2	3	0	1	1	54	53	1680	17	50	63	66	34
F-5	1	0	4	4	2	35	72	2	3	0	1	0	62	61	1710	20	56	67	70	37
F-6	1	1	2	3	5	52	51	0	2	0	0	1	53	76	472	10	13	39	40	17
F-7	1	1	2	4	2	33	48	1	2	0	1	0	58	73	414	14	17	36	68	14
F-8	0	0	1	5	2	35	48	1	2	0	1	1	109	127	1040	18	27	69	94	22
F-9	0	0	1	6	3	39	55	1	2	0	1	2	118	137	1210	20	30	77	126	22
F-10	0	0	1	5	4	56	70	1	1	0	1	1	107	120	856	23	60	93	96	25
F-11	0	0	1	4	4	52	65	1	1	0	1	1	100	110	629	25	57	83	55	31
B-12	1	1	3	4	4	72	97	1	2	0	0	2	114	132	294	11	22	50	62	22
B-13	1	1	2	3	4	60	75	1	1	0	1	3	109	120	264	7	35	51	77	20
B-14	1	2	2	5	3	48	65	2	3	0	2	1	91	110	252	17	35	60	68	14
B-15	1	0	2	5	3	48	66	1	3	0	1	1	103	112	268	12	30	59	49	20
B-16	1	0	2	5	3	50	66	1	3	0	1	2	95	111	296	12	35	60	75	14
B-17	1	3	5	5	3	64	88	0	1	0	0	1	87	99	419	12	16	39	52	17
B-18	1	2	4	5	3	60	82	1	1	0	0	1	76	93	404	9	18	37	56	20
S-19	0	1	3	6	3	54	71	0	1	0	1	1	96	110	584	18	61	94	44	21
S-20	0	1	4	7	3	58	79	1	1	0	1	0	90	93	570	27	138	189	45	21
S-21	0	1	2	6	3	40	54	1	1	0	1	1	102	110	273	12	44	60	43	17
S-22	0	1	2	7	2	39	56	0	1	0	1	1	105	117	322	12	44	71	72	14
S-23	1	1	1	6	3	24	38	1	1	0	1	1	55	66	448	9	42	84	41	17
S-24	0	1	3	5	2	20	34	0	2	0	1	1	53	57	420	7	34	70	44	17
S-25	0	1	3	6	3	29	44	0	2	0	1	1	69	85	430	21	53	61	86	20
S-26	0	1	2	5	2	23	35	0	1	0	0	1	65	68	298	10	36	65	28	14
S-27	0	1	1	4	1	17	26	0	1	0	1	1	43	53	394	11	21	41	48	14
S-28	0	1	2	6	3	33	48	0	2	0	1	1	79	86	367	14	46	65	79	14
S-29	0	1	1	4	2	24	34	0	2	0	1	0	59	73	376	7	35	48	102	14
S-30	0	0	1	1	0	10	13	0	1	0	0	0	25	24	964	24	30	28	79	10
S-31	0	0	0	0	0	7	8	0	1	0	0	0	9	15	792	23	18	30	132	10
S-32	0	1	3	6	3	41	57	0	1	0	1	1	121	137	641	31	75	76	103	20
S-33	0	3	3	7	4	54	75	0	2	0	1	1	58	63	823	49	172	145	239	14

average(X) and standard deviation(σ)

Element	Li							Rb							P	Co	Ni	Cr	Cu	Cs
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
X(F)	1	0	2	3	3	35	47	1	2	0	1	1	69	80	896	16	33	55	63	22
σ (F)	0	0	1	2	2	17	23	1	1	0	1	0	33	37	461	7	20	24	34	9
X(B)	1	1	3	4	3	57	77	1	2	0	1	2	96	111	314	11	27	51	63	18
σ (B)	0	1	1	1	1	9	12	1	1	0	1	1	13	13	69	3	8	10	11	3
X(S)	0	1	2	5	2	31	45	0	1	0	1	1	69	77	513	18	57	75	79	16
σ (S)	0	1	1	2	1	16	21	0	1	0	0	0	31	34	210	11	43	42	53	4
X(T)	0	1	2	4	3	38	52	1	2	0	1	1	75	85	599	16	42	63	70	18
σ (T)	0	1	1	2	1	18	24	1	1	0	1	1	30	34	372	9	33	33	41	6