

GEOCHEMICAL FEATURES OF AQUATIC ENVIRONMENT IN CRATER AND BARRIER LAKES IN NORTHEAST OF CHINA

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(Received 1 May 1998)

ABSTRACT: There are many crater and barrier lakes formed by volcanic activity in northeast of China. These lakes are very rich in fresh water resource. This paper reports systematically geochemical features of some elements in water and sediment in crater and barrier lakes, and discusses the vertical changes, seasonal variation of some elemental concentrations in the lake water and the correlation and the moving coefficient of some elements in sediment. The result shows that the concentrations of Na, Rb, Cs, K, Be, W and F in the crater lake water are higher than those in the barrier lake water, the concentrations of Pb and La are higher and the concentrations of V, Co and Ba are lower in the crater lake sediment than in the barrier lake sediment. Moreover, the concentrations of elements in the lake water and sediment are effected strongly by the lithological characters of the catchment; on the other hand, the biogeochemical effect also acts as an important role.

KEY WORDS: crater lake, barrier lake, water and sediment, geochemical feature, northeast of China

I. INTRODUCTION

Most volcanoes are distributed in northeast of China. The volcanic eruptions can change the general morphologic configuration of the volcanic surroundings and form special volcanic landforms. Precipitation and runoff are stored in craters and form crater lakes. At the same time, the lava blocks up the river valley to form barrier lakes. There are twenty crater and barrier lakes, most of which are distributed in the Changbai Mountains and the Dedu Volcano Group's area in northeast of China. While crater lakes are centralized on Baitou Mountain (the top the Changbai Mountains) and Longgang Mountain (the branch range of the Changbai Mountains). However, Tianchi Lake is the most typical and biggest one among them. Tianchi Lake lies on the border of P. R. China and the Democratic People's Republic of Korea

(DPRK). Its surface appears elliptical, 4850 m from south to north and 3350 m from east to west with 21.4 km² of catchment area, 9.82 km² of water surface area, 373 m of the maximum depth, and 20.4×10^8 m³ of total water quantity. Alkali trachyte, rhyotaxitic trachyte, tuff and zeolitic volcano ash are the main rock types in the catchment basin. Albite, hornblende and oligoclase are the main mineral components of the rock, and main chemical compositions in rocks are Na and K. The geochemical environment belongs to weathering and leaching type with scarce vegetation. Also, there are many parasitic craters on the giant volcano cones of the Baitou Mountain. These small crater lakes, such as Yuanchi Lake, Wangchi Lake, Yinhuan Lake and Qixing Lake, etc. are surrounded by flourishing forests.

On Longgang Mountain, the crater lakes with a water surface area of 0.05–0.73 km² and 20–145 m in depth are Dalongwan Lake, Erlongwan Lake, Sanjiaolongwan Lake, Longquanlongwan Lake, Sihailongwan Lake, Donglongwan Lake, Nanlongwan Lake and Xiaolongwan Lake, etc., and they are forest lakes affected by little human activities.

The barrier lakes formed by the volcano activities are Jingpo Lake, Wudalianchi Lake and Dalinuoer Lake in northeast of China. Jingpo Lake lies on the upper reaches of the Mudan River, with a water surface area of 90.3 km², storage 12.43×10^8 m³, 45 km from south to north and 0.76 km from east to west. The barrier dike formed by volcano eruption in the Quaternary Period is 40 m wide and 12 m high. The catchment has dense vegetation and soil erosion is very light. At present, tourism, hydroelectricity, aquaculture, controlling flood and irrigation are its main functions. Wudalianchi Lake with a total storage of 1.7×10^8 m³ was taken by the lava of volcano eruption within 1719–1721, which barriered the Baihe River and formed five lakes like a string of beads. Among them Sanchi Lake is the biggest and Touchi Lake is the smallest. Aquaculture and tourism are its main functions at present. Dalinuoer Lake was formed by the lava of volcano eruption damming the Kongur River.

The crater and barrier lakes in northeast of China are all fresh water lakes and their total storage is 36.6×10^8 m³. The crater lakes are poor in nutrition, with clear water and rare aquatic organisms, and their water supply mainly comes from groundwater, runoff and precipitation. Because of the luxuriant vegetation, good eco-environment, various animals and plants, resourceful water and many hot springs, they have been becoming landscape tourist and good recreation sites.

II. THE GEOCHEMICAL FEATURES OF ELEMENTS IN CRATER AND BARRIER LAKES

The dominant anion is HCO₃⁻ and dominant cation is Na⁺ or Ca²⁺ in the water of crater and barrier lake in northeast of China. The mineralization degree in the crater lakes (200–300 mg/L) is higher than that in the barrier lakes (< 100 mg/L). The water chemical types are HCO₃⁻ – Na⁺ in the crater lakes and HCO₃⁻ – Ca²⁺ in the barrier lakes.

1. The Concentration Level of Elements in Lake Water

The median concentrations of 36 chemical elements are shown in Table 1. It is obvious that the concentrations of alkali metal elements (Na, Rb, Cs, K) and Be, W, U are higher, but Sr, Sc and As are lower in the crater lakes than those in the barrier lakes. On the other hand, the concentrations of Rb, Cs, Na, Hg, Yb and Ni are higher, but Fe, Cd, As, Se and Sm are lower in the crater lakes than the median content of fresh water in the world (Förstner *et al.* , 1979) and the concentrations of other elements in the crater lakes are equivalent to the median content of fresh water in the world.

Table 1 Elemental concentrations in water of the crater lakes and barrier lakes in north east of China (μg/L)

Elements	Crater lakes	Barrier lakes	Fresh water in the world	Elements	Crater lakes	Barrier lakes	Fresh water in the world
Cu	4. 2	2. 8	2. 0	Ba	8. 6	19. 2	10. 0
Pb	1. 1	1. 0	0. 2	Sc	0. 003	0. 016	0. 010
Zn	11	12	15	W	3. 07	0. 31	
Cd	0. 008	0. 012	0. 070	Sb	0. 15	0. 21	0. 20
Co	0. 11	0. 10	0. 20	K*	3. 89	1. 23	
Ni	1. 0	1. 4	0. 3	Na*	25. 72	2. 91	
As	0. 76	2. 85	2. 00	Ca*	9. 4	8. 1	
Hg	0. 046	0. 054	0. 010	Mg*	0. 96	1. 65	
Cr	0. 33	0. 26	0. 50	Cl*	14. 42	6. 93	
Se	0. 15	0. 09	0. 20	La	0. 14	0. 15	0. 10
Mo	1. 15	1. 08	0. 50	Ce	0. 15	0. 16	0. 20
V	1. 2	2. 4	0. 9	Sm	0. 013	0. 025	0. 060
Mn	6. 3	3. 1	5. 0	Eu	0. 008	0. 010	0. 006
Fe	49	142	500	Tb	0. 006	0. 005	0. 003
Rb	27. 7	2. 1	1. 0	Yb	0. 031	0. 013	0. 010
Cs	1. 40	0. 04	0. 02	Lu	0. 002	0. 005	0. 003
Be	4. 90	0. 03		U	0. 32	0. 09	0. 40
Sr	32	99	70	Th	0. 013	0. 018	0. 030

* mg/L

2. The Seasonal Variation of Elemental Concentrations in Lake Water

In various seasons, the differences in temperature, precipitation, vegetation and hydrology bring about different functions of leaching, removing, exchanging and transforming of elements in lake water, thus affecting the concentrations of elements in lake water. The concentrations of chemical elements during median water period and low water period in Sanjiaolongwan Lake show that Mo is obviously higher during median water period (0. 32 μg/L) than that during

low water period (0.03 $\mu\text{g/L}$), but the concentrations of Cu, Pb and Zn have no marked difference between the two periods. During median water period, the higher temperature leads microorganism to decompose vegetation remains fast, and the organic material decomposed is moved easily into the lake water by surface runoff. So, the concentration of organic material is higher during median water period than that during low water period. Mo may have something to do with the action of organic matter.

The elemental concentrations in lake water in northeast of China are mainly affected by the components of soil, precipitation and groundwater. At the same time, deep water, small basin and long water cycle period lead to the feeble exchanging function of lake water. Consequently, the elemental concentrations in lake water are stable in a long period, especially in crater lakes. The elemental concentrations in surface water of Tianchi Lake surface water during median water period in different years (She *et al.* , 1992) can explain these phenomena (Table 2).

Table 2 Elemental concentrations in water of Tianchi Lake ($\mu\text{g/L}$)

Elements	1984	1979	Elements	1984	1979
As	1.60	0.93	Rb	62.0	49.0
Zn	11.0	11.8	Cs	3.6	2.6
Cr	0.25	0.31	U	0.61	0.33
Fe	34.0	31.0	Sb	0.29	0.27
Co	0.16	0.17	Sc	0.006	0.0057
Na*	57.0	54.0	Se	0.07	0.13
Ca*	11.0	12.4	Ce	0.17	0.11
Ba	4.0	7.2	Sm	0.02	0.05

* mg/L

3. The Vertical Changes of Elemental Concentrations in Lake Water

Because of the effects of depth of lake water, the pattern of water supply, exchanging function and biological activity, the elemental concentrations in lake water present vertical changes (Zhu *et al.* , 1981). Consequently, from surface to deep layer, pH value varies from 8.16 to 7.29, and dissolved oxygen (DO) from 10 mg/L to 8 mg/L. In the meantime, the concentrations of main ions K^+ , Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- are ascend and Sr, Ba, Zn and Fe are descend along with increment of water depth. In Jingpo Lake, because of dramatic biogeochemical action and strong biological activity in sediments, methylmercury concentration in lake water is obviously higher in bottom layer than that in surface layer.

4. The Difference of Elemental Concentrations in Different Lake Water

Because of the differences in rock, soil, surface material, hydrology, water supply in dif-

ferent catchment basins, the elemental concentrations in lake water are obviously different. The elemental concentrations in Sanjiaolongwan Lake, Longquanlongwan Lake and Tianchi Lake during median water period are shown in Table 3. The concentrations of Zn and Mo are higher in Tianchi Lake, FA(fulvic acid), Cu and Pb are higher in Longquanlongwan Lake, while Zn is lower in Sanjiaolongwan Lake than those in other lakes. Obviously, those phenomena are because that there are low altitude, evident biochemical action, farming and forest in Longquanlongwan Lake basin, but there are exposed volcanic ash and evident geochemical action in Tianchi Lake basin. Moreover, the differences of elemental concentrations between crater lake water and barrier lake water are also obvious. For example, mercury concentration is higher in barrier lake water than that in crater lake water. That is, mercury, especially methylmercury concentration is obviously high in the lake water with evident biochemical action (Table 4).

Table 3 Difference of elemental concentrations in lake water($\mu\text{g/L}$)					
Lake	FA	Mo	Cu	Pb	Zn
Tianchi Lake	0.56	4.65	4.4	1.1	14.3
Longquanlongwan Lake	7.33	1.02	7.2	5.2	2.1
Sanjiaolongwan Lake	0.38	0.32	2.0	0.7	15.3

Table 4 Hg concentrations in lake water ($\mu\text{g/L}$)				
Lake	Total Hg	Suspend Hg	Dissolved Hg	Methylmercury*
Tianchi Lake	0.040	0.024	0.016	0.08
Jingpo Lake	0.044	0.030	0.014	0.18
Wudalianchi Lake	0.067	0.047	0.020	0.10
Longquanlongwan Lake			0.036	0.29

* ng/L

III. THE GEOCHEMICAL FEATURE OF ELEMENTS IN LAKE SEDIMENT

1. The Elemental Concentrations in Lake Sediment

The concentrations of 20 elements in sediment are shown in Table 5. Pb and La are obviously higher but V, Ca and Ba are obviously lower in the crater lake sediment than those in the barrier lake sediment, and other elements are equivalent in the two kinds of sediments. Except for As, Sr, Mo in the crater lake sediment and K, Co, Cr, V, Fe, Ba, Sr and La in the barrier lake sediment, the ranges of other elemental concentrations are quite great, and the ratio of the highest concentration to the lowest one is more than 3, especially, the ratio of Ni in the crater lake sediment is 43 and Zn in the barrier lake sediment is 32.

Table 5 Elemental concentrations in sediment of lakes (mg/kg)

Elements	Crater lakes		Barrier lakes	
	range	average value	range	average value
K	$7.60 \times 10^3 - 5.24 \times 10^4$	2.89×10^4	$1.35 \times 10^4 - 3.04 \times 10^4$	2.04×10^4
Na	$5.00 \times 10^3 - 4.24 \times 10^4$	2.27×10^4	$6.00 \times 10^3 - 2.33 \times 10^4$	1.27×10^4
Ca	$4.20 \times 10^3 - 1.20 \times 10^4$	6.80×10^3	$4.30 \times 10^3 - 1.94 \times 10^4$	7.90×10^3
Mg	$1.20 \times 10^3 - 1.03 \times 10^4$	5.30×10^3	$1.20 \times 10^3 - 1.14 \times 10^4$	7.60×10^3
Cu	11- 53	27	10- 56	33
Pb	6.15- 64	31.53	0.36- 34.6	12.2
Zn	57- 167	111	20- 650	160
Cd	0.24- 1.27	0.53	0.03- 0.73	0.30
Co	1- 21	8	9- 23	17
Ni	5- 217	53	18- 60	37
As	4- 10	5.45	3.4- 13	9.61
Hg			0.002- 0.062	0.042
Cr	10- 130	46	42- 93	70
V	14- 137	50	70- 137	107
Mn	149- 1339	829	445- 2307	1108
Fe	$1.3 \times 10^4 - 5.1 \times 10^4$	3.66×10^4	$2.84 \times 10^4 - 5.76 \times 10^4$	4.42×10^4
Mo	10- 28	14		
Ba	52- 561	226	660- 880	787
Sr	23- 57	39	33- 95	61
La	30- 323	121	43- 55	46

2. The Relation Analysis Among Elements in Lake Sediment

For the sake of studying the relation among elements, the correlation matrix analysis between 13 elements in the barrier lake sediment are computed(Table 6) . The result shows that the correlation coefficients among Pb, Cd, Co, Ni, Fe, Hg, Cr and Zn are very high, and appear strong positive relation under significance level of 0.001. On the other hand, the correlation coefficients of Zn- Cu, Zn- Pb, Zn- Cd, Hg- Cu, Hg- Pb, Hg- Cd, Mn- Co, Mn- Ni, Mn- Fe, Cr- Pb, Cr- Cd, Sr- Ni are high($\alpha= 0.05$) , but Sr has negative relation with most elements, As and Ti have little relation with other elements. The result proves strong relations among the same pedigree elements and the elements with similar electron outer-ring structure.

3. The Effects of Rock and Soil on the Elemental Concentrations in Lake Sediment

Lake sediment mainly originates from rock pieces, weathered material and soil particle, so elemental concentrations in sediment are the synthetical reflecting of elemental concentrations in rock and soil of a basin. Table 6 lists the elemental concentrations of sediment and rock or soil

Table 6 Correlation matrix of elements in the barrier lake sediment

Element	Cu	Pb	Zn	Cd	Co	Ni	As	Hg	Cr	Fe	Mn	Sr	Ti
Cu	1.000		++					++	+				
Pb	0.607	1.000	++	+++				++	++				
Zn	0.886	0.856	1.000	++				+++	+++				
Cd	0.675	0.970	0.892	1.000				++	++				
Co	0.225	-0.426	-0.211	-0.148	1.000	+++				+++	++	-	
Ni	0.298	-0.401	-0.125	-0.394	0.976	1.000				+++	++	--	
As	0.241	-0.114	-0.054	-0.050	0.343	0.297	1.000						
Hg	0.885	0.844	0.995	0.894	-0.239	-0.149	0.008	1.000	+++				
Cr	0.762	0.873	0.957	0.858	-0.376	-0.268	-0.119	0.953	1.000				
Fe	0.196	-0.535	-0.265	-0.504	0.981	0.967	0.425	-0.279	-0.424	1.000	++	-	
Mn	0.520	-0.224	0.114	-0.156	0.882	0.859	0.285	0.086	-0.103	0.873	1.000	-	
Sr	-0.555	0.269	-0.169	0.218	-0.727	-0.820	-0.463	-0.179	-0.070	-0.795	-0.763	1.000	
Ti	-0.445	-0.140	-0.409	-0.322	0.248	0.251	-0.338	-0.463	-0.306	0.134	-0.146	0.185	1.000

Notes: Positive correlation: +++ $\alpha = 0.001$, ++ $\alpha = 0.01$, + $\alpha = 0.05$;

Negative correlation: --- $\alpha = 0.001$, -- $\alpha = 0.01$, - $\alpha = 0.05$

in Tianchi Lake and Jingpo Lake basins. The elemental concentration order of sediment in Tianchi Lake is $\text{Fe} > \text{Na}, \text{K} > \text{Ca} > \text{Mn} > \text{Mg} > \text{Zn} > \text{Cu} > \text{Pb} > \text{Cr} > \text{Co}, \text{Sr} > \text{Ni}, \text{Mo} > \text{Cd}$, elemental concentration order in rock is similar to the order in sediments except for Cu, Mn, Zn and K. On the other hand, the elemental concentration orders both in sediment and soil in Jingpo Lake basin are $\text{Fe} > \text{Ti} > \text{Mn} > \text{Sr} > \text{Zn}, \text{Cr} > \text{Ni} > \text{Cu} > \text{Co} > \text{Pb} > \text{As} > \text{Cd} > \text{Hg}$. Meanwhile, the elemental concentrations (except K and Na) in sediment are higher than those in rock in Tianchi Lake basin, and the elemental concentrations (except Sr, Hg and Ti) in sediment are higher than those in soil in Jingpo Lake basin. This proves not only sufficiently accordance of the elemental composition in sediment with that in surface material of basin, but also that leaching is the main process when the easy resolved elements transport into the lake water. Grain material has an accumulation action to the difficultly resolved elements, biotic action can change the distribution of some elements (such as Hg) in waterbodies, too.

The result also indicates that the ratio of the elemental concentrations in the sediment to that in the rock of basin in Tianchi Lake is obviously higher than that in Jingpo Lake, this manifests that the accumulation of some elements in sediment relates to not only physical, chemical and biotic actions, but also the inflow of warm springs.

4. Element Transportation and Transformation in Sediment

The elemental concentrations in water and sediment are closely related. Fig. 1 and Fig. 2 indicate respectively that the elemental concentrations in water have similar distribution trend with those in sediment, but the elemental concentrations in sediments is 10^2 – 10^5 times higher

than those in the water, this indicates that the elements in lake are mainly accumulated in sediment. Clark value (K) is used to show the accumulation and dispersion degree of elements in sediment. K is the ratio of the elemental concentration in sediments to that in the crust. If $K < 1$, the element is dispersed in the sediment. If $K > 1$, the element is accumulated. The result (Table 7) indicates that Mn, Sr, Ni, Cr and Co in Tianchi Lake sediment are dispersed, especially Sr and Mn are dispersed greatly; other elements are accumulated, the accumulation coefficients of K, Na, Ca, Mg, Fe, Pb, Mo and Cd are comparatively high. Cu, Sr, Ni, Co, Cr, Fe, Ti and Pb are dispersed, and Hg, As, Cd, Mn and Zn are accumulated in Jingpo Lake; but the accumulation and dispersion degree are much lower than those in Tianchi Lake sediment. The elemental accumulation and dispersion in lake sediment are mainly determined by elemental concentrations in the rock or soil of the basin.

Table 7 The relationship of elemental concentrations between sediments and rock or soil of basin in Tianchi Lake and Jingpo Lake(mg/kg)

Tianchi Lake					Jingpo Lake				
Elements	Sediment (A)	Rock (B)	A/B	K	Elements	Sediment (C)	Soil (D)	C/D	K
Cu	182	12.6	14.4	3.31	Cu	22.4	19.8	1.1	0.41
Pb	131	42	3.1	10.48	Pb	12.1	9.64	1.3	0.97
Zn	331	51	6.5	4.73	Zn	84.6	67.2	1.3	1.21
Cd	2	2	1	10	Cd	0.48	0.47	1.0	2.40
Co	22.2	11.9	1.9	0.89	Co	16.4	13.3	1.2	0.66
Ni	15	6.7	2.2	0.2	Ni	39.3	26.3	1.5	0.52
Cr	33	11	3	0.33	Cr	82.8	67.8	1.2	0.83
Fe	3.33×10^4	3.03×10^4	1.1	59.22	Fe	5.32×10^4	3.55×10^4	1.5	0.94
Mn	4.75×10^3	6.2×10^2	7.7	0.05	Mn	1.36×10^3	9.97×10^2	1.4	1.43
Sr	22			0.06	Sr	179	250	0.7	0.48
K	3.01×10^4	8.82×10^4	0.3	143.83	Ti	5.15×10^4	5.41×10^4	0.95	0.90
Na	3.08×10^4	3.99×10^4	0.8	130.59	As	7.28	4.18	1.7	4.04
Ca	5.65×10^3	2.60×10^3	2.2	24.25	Hg	0.113	0.168	0.7	14.13
Mg	2.4×10^3	2.0×10^3	1.2	5.78					
Mo	14.11	5.73	2.5	9.41					

IV. CONCLUSIONS

Through above-mentioned analysis, we can draw the following conclusions:

- 1) Many crater lakes and barrier lakes are distributed in northeast of China, fresh water resource stored in them is plentiful($36.6 \times 10^8 \text{ m}^3$) and the water quality is good because it is affected lightly by human activities.
- 2) The mineralization degree of the crater lake water(200– 300 mg/L) is rather higher than that in the barrier lakes(< 100 mg/L), and the water chemical type is mainly HCO_3^- –

Na^+ in the crater lakes and $\text{HCO}_3^- - \text{Ca}^{2+}$ in the barrier lakes. The concentration of Na, Rb, Cs, K, Be, W and F in crater lake water is obviously higher, while Sc, Sr and As is obviously lower than those in barrier lake water.

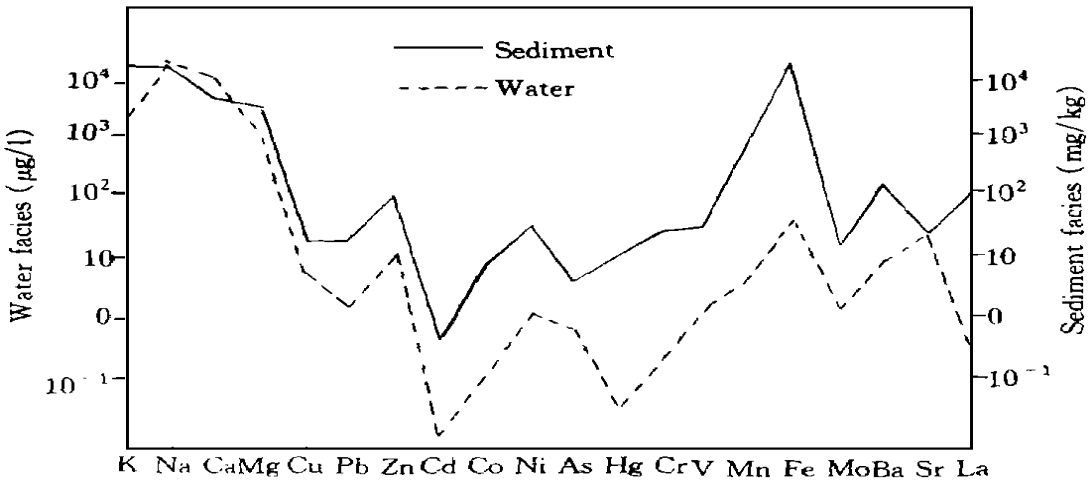


Fig.1 The distribution of elemental concentrations in water and sediment of crater lakes

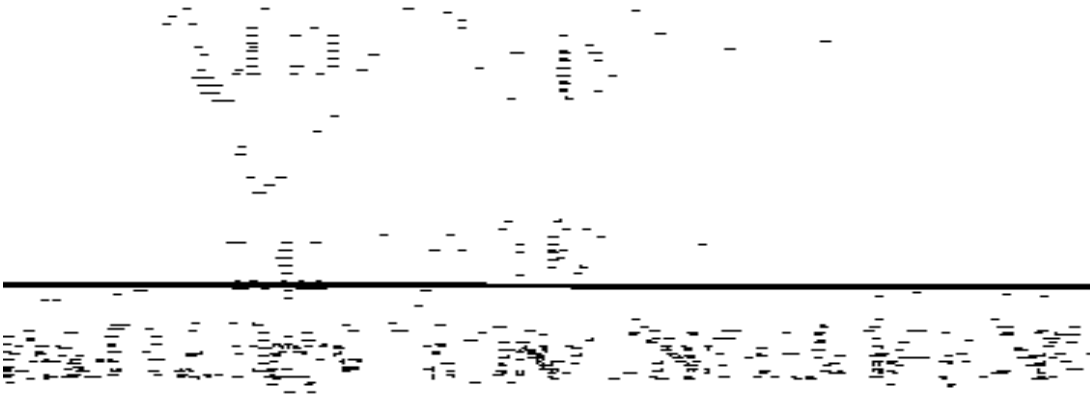


Fig. 2 The distribution of elemental concentrations
in water and sediment of barrier lakes

- 3) Most elemental concentrations have not obviously seasonal variation in lake water, but some elements have vertical differences in concentration.
- 4) The concentrations of Pb and La in crater lake sediment are higher than those in barrier lake sediment, while the concentrations of V, Co and Ba in crater lake sediment are lower than those in barrier lake sediment, the strong positive correlations appear among Pb, Cd, Hg, Zn, Cr, Co, Ni and Fe; Sr has negative correlation with most other elements, while As and Ti correlate weakly with other elements; most elemental concentrations in sediment are higher than those in rock or soil of the lake basin, the accumulation and dispersion degree in crater lake sed-

iment are higher than those in barrier lake sediment.

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