

# Composition, spatial distribution, and environmental significance of water ions in Pumayum Co catchment, southern Tibet

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**Abstract:** The chemistry of major cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ , and  $K^+$ ) and anions ( $HCO_3^-$ ,  $SO_4^{2-}$ , and  $Cl^-$ ) in the water of Lake Pumayum Co and its inflow river was studied, revealing the obvious ionic difference among various inflow rivers and the lake. The chemical type of the lake water was  $Mg^{2+}-Ca^{2+}-HCO_3^- -SO_4^{2+}$ , but the major ions of the main inflow rivers were  $Ca^{2+}-Mg^{2+}-HCO_3^-$ . In the lake inlet of Jiaqu River, the main inflow river, there was significant variance of water chemistry within the depth less than 2 m. However, it was almost homogeneous at other area of the lake. Therefore, with the evidence of distribution of water chemistry and oxygen isotope of lake water, a conclusion can be outlined that Jiaqu River had a distinct effect on the hydrochemistry of the water on the submerged delta, whereas this is not the case for other rivers. The Gibbs plot revealed that the dominant mechanism responsible for controlling chemical compositions of the lake water was rocks weathering in the drainage area. Ion ratios and ternary plots further explored the main processes controlling the water chemistry of the catchment, i.e., carbonate weathering, pyrite weathering, and silicate weathering. The different hydrochemistry characteristics between river water and lake water may result from the  $CaCO_3$  precipitation. The findings will benefit the explanation of the environmental significance of carbonate in paleolimnological studies in the lake.

**Keywords:** Lake Pumayum Co; hydrochemistry; spatial distribution; sedimentary process; carbonate

Most lakes on Tibetan Plateau are endorheic. Various environmental proxies reflecting changes of lakes themselves and climate can be reserved to the fullest extent in the lake sediments and their basins, which benefits those studies such as the history of climate changes in different time scales, water/thermal conditions in different stages, and the pa-

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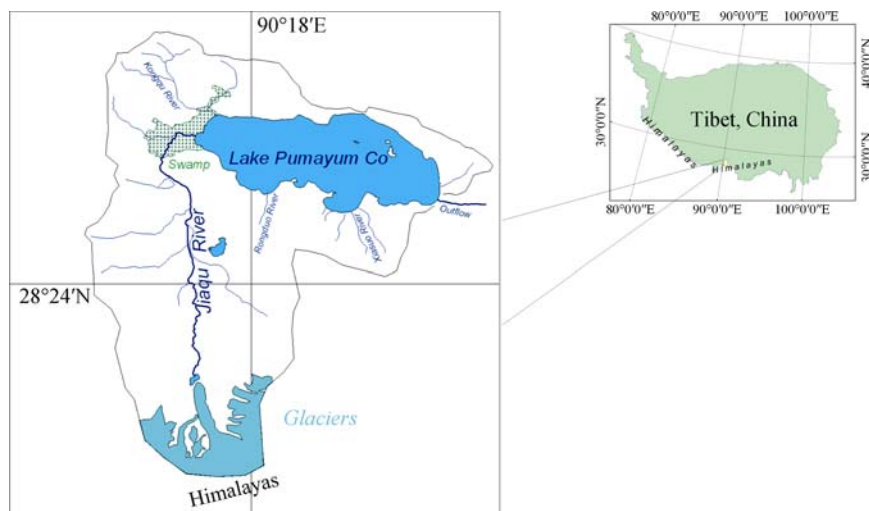
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leocology features (Zhu *et al.*, 2006). The hydrochemistry of a lake, supplied by surface inflows or/and precipitation, can be influenced by tectonic activity and rock weathering of its catchment (Hem and John, 1985; Stallard and Edmond, 1983), climatic changes (Chen *et al.*, 2000), and human activities (Wang and Dou, 1998). The ion composition is a significant aspect of hydrochemical characteristics. Therefore, the study on the ionic character of the lake and rivers of a catchment can benefit comprehending the supply of rivers to the lake and the ion composition and origin of the lake water. Many studies used elements of lake sediments as proxies in paleoenvironmental changes study on the Tibetan Plateau. For example, in Lake Chen Co of south Tibet and south Hongshan Lake of northwest Tibet, Zhu *et al.*, (2002; 2004) used elements of C, N, Fe, Mn, Sr, and Ba as proxies; in central Tibet, Gu *et al.* (1994) used alkali elements in Lake Siling Co and Wu *et al.* (2001) used carbonate, isotopes, and Ca, Mg, Sr of ostracode shells in Lake Co Ngoin to reconstruct past environment. However, most work just utilized the results of studies in other lakes. Therefore, due to the significant regional variation of lake deposition, the study on ions of lake water can benefit comprehending the origin of them, and thereafter the spatial extent of environmental significance of lake sediments and the study on the modern sedimentary process.

Lake Pumayum Co is located in the south of the Tibetan Plateau, where the limnological study, not only on environmental changes but on other aspects, is comparatively insufficient. In this paper, the hydrochemical characteristics and the source and the dominant processes controlling main ions composition were mainly discussed, which also provides fundamental data for the study on lake sedimentary processes.

## 1 Study area

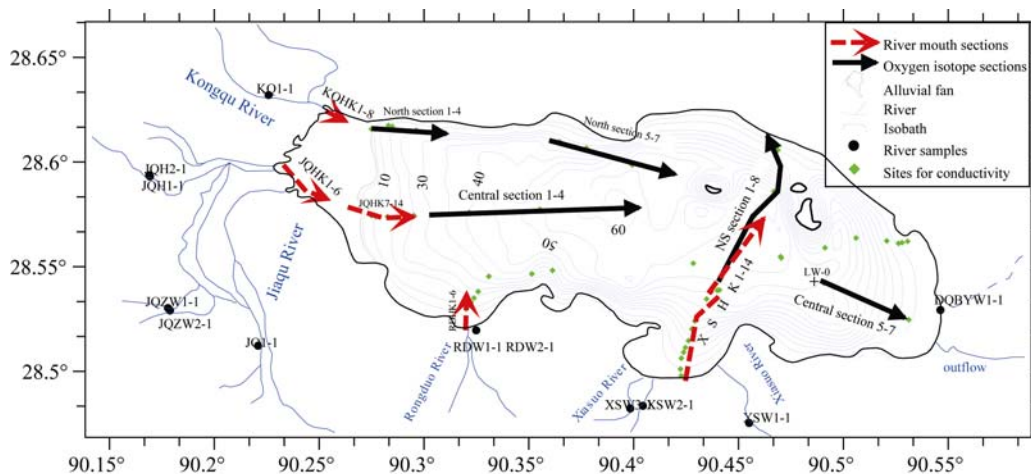
Lake Pumoyum Co ( $28^{\circ}30' - 28^{\circ}38'N$ ,  $90^{\circ}13' - 90^{\circ}33'E$ , altitude 5030 m a.s.l.), is located in a mountain basin in the pre-Himalayas of Tibet (Figure 1). It is a semi-enclosed lake with a water surface of  $290 \text{ km}^2$  in a catchment area of  $1232.9 \text{ km}^2$ . The recharge coefficient is 4.2 and the development coefficient is 1.56 (Wang and Dou, 1998). There are four inflowing rivers around the lake, of which the Jiaqu River is the maximal, deriving from the melting



**Figure 1** Location of Lake Pumayum Co and the morphometry of its catchment (Ju *et al.*, 2009)

water in the south of the lake and accounting for 77% of all inflows (Zhu *et al.*, 2006). The climate of the lake area is upland brushy grassland semiarid climate in south Tibet with an annual mean temperature of 2–4°C and annual precipitation of 300 mm (Wang and Dou, 1998).

In the west side of the lake, there is a submarine alluvial fan with a water depth of less than 4 m, induced mainly by Jiaqu River (Figure 2). On that fan, water with a depth less than 2.6 m looks as turbid as Jiaqu River. However water becomes clear after passing the 2.5–2.6 m isobath and looks bright green. There is a newly excavated open channel on the east side, through which water joins the river flowing into Lake Yamzhoyum Co, located about 40 km northward to Lake Pumayum Co, during high lake level period. Geologically, the whole catchment belongs to Upper Triassic ( $T_3ny$ ) (Bureau of Geology and Mineral Resources of Xizang Autonomous Region, 1993), where limestone, shale, and sandstone can be found. Pluvial-alluvial plains are distributed to the east, south, and west shorelines of the lake while the north lakefront is a fault scarp. Under the actions of Quaternary glaciations, moraines are widely distributed in mountain valleys while Quaternary loose accumulated materials are observed elsewhere from piedmont to lake shorelines (Li *et al.*, 1983). Pluvial-alluvial plains are distributed to the east, south and west shorelines of the lake while mountains foot arrived at its north bank (Wang and Dou, 1998).



**Figure 2** Bathymetry of Lake Pumayum Co and sampling sites. Numbers of JQHK, KQHK, RDHK and XSHK indicate the samples from each river mouth to the inner lake respectively

## 2 Materials and methods

Lots of water samples were collected in 2005, including 12 water samples taken from every inflowing river and surface water samples collected at 45 sites of different depths along four track lines from each river mouth to the inner lake (Figure 2). By using a multiprobe sensor (Hydrolab DS5), water temperature, pH, specific conductivity (SpCond), photosynthetically active radiation (PAR), and concentration of luminescent dissolved oxygen (LDO) were measured *in situ* at 58 sites all over the lake (Figure 2). Twenty-two surface water samples were collected along three sections. Those lake samples and Jiaqu River samples were used

for the measurement of  $\delta^{18}\text{O}$ .

Major cations of water samples collected in 2005 were determined with another ion chromatograph (ICS-2500, Dinex) and major anions except  $\text{HCO}_3^-$  were measured by ICS-2000.  $\text{HCO}_3^-$  concentration was estimated from the ion balance of major cations and anions. Oxygen isotope of Jiaqu River and some lake water were measured by MAT 253, based on the  $\text{CO}_2\text{-H}_2\text{O}$  equilibrium method, with a precision of 0.2‰.

### 3 Results and discussion

#### 3.1 Main ions and total dissolved solids (TDS)

The major cations in the water of broad area of Lake Pumayum Co are in decreasing order as  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ \gg \text{K}^+ > \text{Sr}^{2+}$  and the major anions are also in decreasing order as  $\text{HCO}_3^- > \text{SO}_4^{2-} \gg \text{Cl}^-$  (Table 1).  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  account for 80% of the major cations.  $\text{Mg}^{2+}$  is the predominant cation, which accounts for 53% of the major cations.  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  are the first and second dominant anions, which account for 73% and 25% of the major anions respectively (Table 1). Therefore, the main cation composition is  $\text{Mg}^{2+}\text{-Ca}^{2+}\text{-HCO}_3^-\text{-SO}_4^{2+}$ , which is consistent with the data in August, 1974 (Guan *et al.*, 1974). TDS varies 251–307 mg/L.

**Table 1** Ion composition (equiv. %) and TDS (mg/L) for water samples from Lake Pumayum Co

Site	$\text{Ca}^{2+}/\text{TZ}^+$		$\text{Mg}^{2+}/\text{Tz}^+$		$(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{TZ}^+$		$\text{HCO}_3^-/\text{TZ}^-$		$\text{SO}_4^{2-}/\text{TZ}^-$		$(\text{Na}^++\text{K}^+)/\text{TZ}^+$		TDS	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Mean	25.99	60.31	53.23	25.66	79.23	85.96	72.67	61.11	25.94	36.79	20.45	13.90	285.60	127.52
Minimum	24.83	32.03	49.11	16.12	77.09	74.33	69.74	27.25	22.26	23.72	18.71	7.67	266.14	48.17
Maximum	29.55	74.85	54.71	48.52	81.16	92.33	76.71	75.31	29.45	64.01	22.63	25.52	307.61	264.40
Number	29	16	29	16	29	16	29	16	29	16	29	16	29	16

Note:  $\text{TZ}^+$  and  $\text{TZ}^-$  stand for total cations and total anions respectively; Sites 1 and 2 refer to the broad lake area and the western alluvial fan of Pumayum Co, respectively.

The ion composition in the water on the western alluvial fan is also considerably different from that of the water on the broad lake area (Table 1).  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  account for 80% of the major cations, but the predominant cation is  $\text{Ca}^{2+}$ , which accounts for about 60%;  $\text{HCO}_3^-$  is still the predominant anion, however, content of  $\text{SO}_4^{2-}$  accounts for as high as 37%. There are considerable spatial variations of TDS on that fan. In the water on the river mouth of Jiaqu River (samples named by JQHK in Figure 2), the TDS is less than 100 mg/L. However, it takes on higher value in the water on the Kongqu River mouth. The ion composition of the former area looks more like inflowing water.

There are great variations among the TDS in different inflows. The TDS of Jiaqu River, the river with biggest flux and velocity, is as low as 54.22 mg/L (JQ1-1). However the TDS of the two streams on the alluvial fan is as high as 540 mg/L (JQH1-1, JQH2-1). Furthermore, the seasonal inflow in the southeast has the TDS as high as 667 mg/L (QBYW1-1). Most of other rivers have the TDS of 100–300 mg/L. While the ion composition of each river displays a uniform, that is, the main cations are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and moreover, the

concentration of  $\text{Ca}^{2+}$  is two or more times of it of  $\text{Mg}^{2+}$ ; the content of  $\text{HCO}_3^-$  accounts for 90% of the anions and the content of  $\text{SO}_4^{2-}$  is much lower than it in lake water.

### 3.2 Mechanisms controlling the major element chemistry of the lake

Three sources have been named by Berner and Berner (1996) as the possible cause of dissolved salts into the inland waters, which include (1) sea salts carried in the atmosphere and deposited in the lake; (2) weathering of silicate, carbonate, evaporite and sulfide minerals, and (3) anthropogenic input. The third source can be ignored for few people living here.

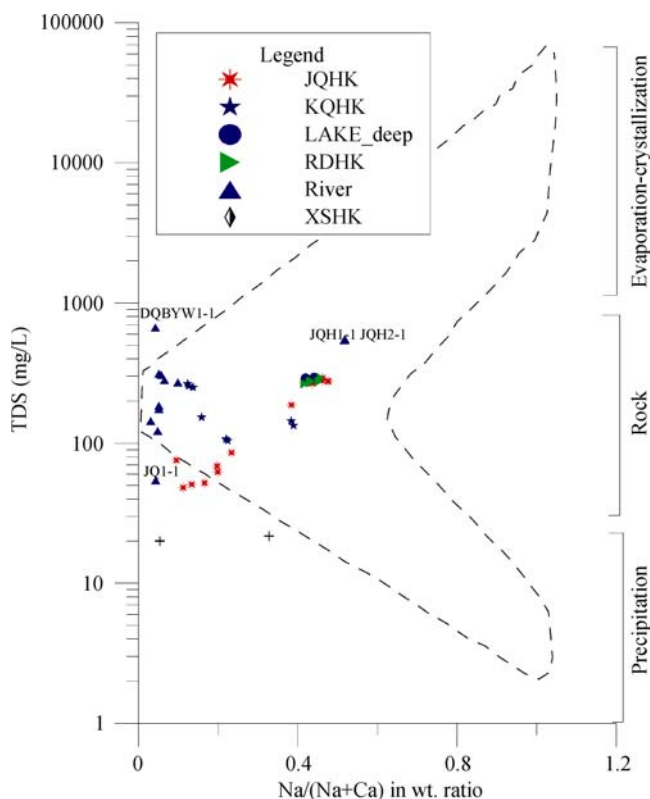
#### 3.2.1 Gibbs plot analysis for the ion source of Lake Pumayum Co water

Gibbs semilogarithmic diagram (Figure 3) is often used to study the major sources of surface waters ions. Plotted in Figure 3 is the weight ratio  $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$  (or  $\text{Cl}^-(\text{Cl}^- + \text{HCO}_3^-)$ ) on the *x*-axis and the variation in TDS on the *y*-axis. The compositions of most of the world's surface waters are plotted in dashed line area on Gibbs diagram (Gibbs, 1970)

Because  $\text{Cl}^-$  concentration in river water of Pumayum Co catchment is less than 0.1% of all anions (from Table 1), almost undetected by instruments, we use the weight ratio  $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$  as the *x*-axis of Gibbs diagram in this paper. Viewed as a whole, the Gibbs diagram displays that the rock weathering dominates the ion composition of waters in the study area. In addition, there are some differences of hydrochemistry among water in inflows, estuary and the center of the lake.

The water samples JQ1-1 (in Jiaqu River) and JQHK (in river mouth of Jiaqu River) are distributed in the low value area of TDS parameter. Due to the high  $\text{Ca}^{2+}$  proportion of the water, samples in shallow water (depth less than 2 m) of Jiaqu River mouth (JQHK) and Kongqu River mouth (KQHK) and most river samples including JQ1-1 (from Jiaqu River), are distributed in the low value area of *x*-axis. Jiaqu River is the largest inflow of the lake. Therefore, the brisk current make hydrochemical composition of the estuarine area (JQHK) is similar to the river (JQ1-1).

The estuarine samples of Rongduo River (RDHK) and Xiasuo River (XSHK) and the



**Figure 3** Plot of TDS versus weight ratio of  $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$  of Lake Pumayum Co and inflow rivers water samples (after Gibbs 1970). Note that the major ion chemistry of the catchment distributed in the rock-dominant field

surface lake water of deep lake (Lake\_deep) area are distributed in the same position of higher  $x$  value, which indicates little influence of the two rivers on the characteristics of the lake water perhaps due to the lower velocity and flux. Conversely, water samples points from Jiaqu River and from Jiaqu River mouth are distributed in the same place in the Gibbs plot (Figure 3), which indicates great influence of Jiaqu River on the characteristics of the lake water due to the high velocity and flux. The different positions of Jiaqu River (JQ1-1) and some little streams (JQH1-1, JQH2-1) in Figure 3 result from the significant difference of TDS. The difference is consistent with the hydrochemical analysis of Muztag Ata glacier area (Zhao *et al.*, 2006) and Tanggulha glacier area (Sheng *et al.*, 1996), that is, the faster the river flow, the shorter the time of the water contacting the riverbed is and the less the soluble salts of the soil and rock release; the larger the flow flux, the more the diluted soluble salt. Those factors result in the decrease of ionic concentration accordingly.

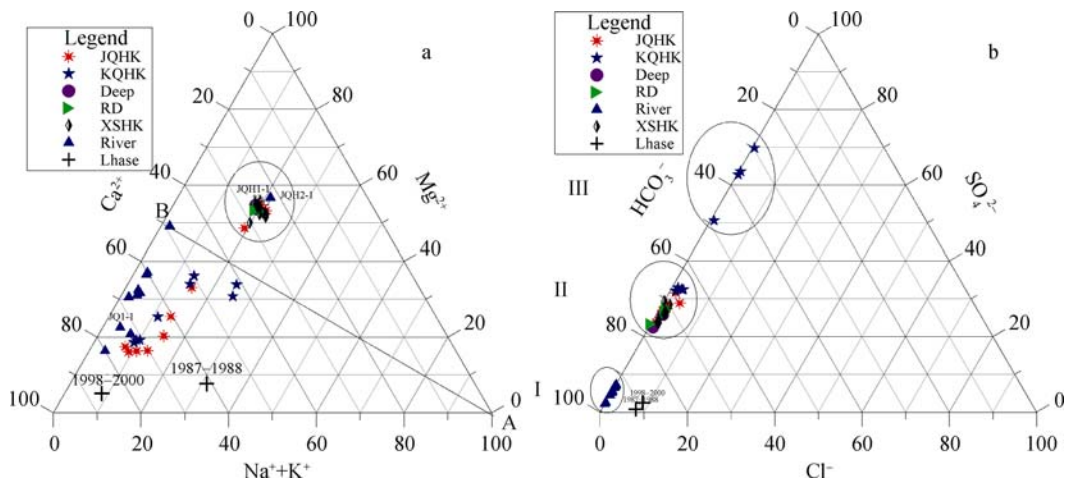
### 3.2.2 Influences of cyclic salts

Gibbs plot has showed that the dominant process influencing the hydrochemistry is rock weathering and no sample dots are located in the precipitation domination. Further discussion can be done by ratios of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$ . Molar ratios of  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  in marine aerosols are 0.8517 and 0.0176 (Zhang *et al.*, 1995). However, in waters of Pumayum Co catchment, the proportion of  $\text{Cl}^-$  in total anions is less than 0.1% (Tables 1 and 2; Figure 4). Ratio of  $\text{Na}^+/\text{Cl}^-$  is as high as tens or hundreds and  $\text{K}^+/\text{Cl}^-$  is more than 1. For example, the ratios in Jiaqu River (with minimal TDS) are 132 and 48. Therefore, the influence of sea salts on the ion composition can be ignored. The average value of hydrochemical composition of multi-year precipitation in Lhasa, which shares the same vapor source (Yin *et al.*, 2006), is used to estimate the influence of precipitation and sea salt on the surface water (Table 2 and Figure 4). Just like water in rivers, the dominant ions are  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , indicating the hydrochemistry of precipitation is mainly influenced by chemical characteristics

**Table 2** Ion composition (equiv. %) and TDS (mg/L) of inflow rivers and precipitation of Lhasa

Name	TDS	$\text{Ca}^{2+}/\text{TZ}^+$	$\text{Mg}^{2+}/\text{Tz}^+$	$(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{TZ}^+$	$\text{HCO}_3^-/\text{TZ}^-$	$\text{Cl}^-/\text{TZ}^-$	$\text{SO}_4^{2-}/\text{TZ}^-$	$(\text{Na}^++\text{K}^+)/\text{TZ}^+$
JQZW1-1	312.10	64.12	32.29	96.41	93.33	0.01	6.64	3.13
JQZW2-1	307.15	65.05	30.96	96.01	93.53	0.01	6.45	3.54
JQ1-1	54.22	73.43	22.60	96.03	97.39	0.02	2.53	3.97
JQH1-1	547.70	22.00	56.37	78.37	93.28	0.08	6.61	21.13
JQH1-2	543.30	22.11	56.35	78.46	93.13	0.08	6.76	21.05
KQ1-1	270.31	71.65	20.80	92.44	93.33	0.01	6.64	7.16
XSW1-1	280.52	64.09	31.47	95.56	94.41	0.02	5.54	4.00
XSW2-1	143.33	67.46	30.61	98.07	95.49	0.01	4.50	1.93
XSW3-1	121.74	79.83	16.34	96.17	97.87	0.02	2.10	3.60
DQBYW1-1	667.61	48.71	49.00	97.72	92.71	0.07	7.21	1.97
RDHW1-1	184.62	59.98	37.08	97.06	94.82	0.05	5.12	2.94
RDHW1-2	174.67	60.49	36.55	97.04	94.63	0.05	5.32	2.96
Lhasa87-88*	14.01	57.43	7.20	64.64	90.69	7.74	0.76	29.26
Lhasa98-00*	13.19	83.24	4.92	88.16	86.44	8.36	2.37	8.19

Note: Lhasa87-88 and Lhasa98-00 stand for 14 precipitation samples of Lhasa in 1987–1988 and 15 precipitation samples of Lhasa in 1998–2000; \*, after Zhang *et al.* (2004).



**Figure 4** Ternary plots showing the relative abundances (in equivalent units). (a) Main cations:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $(\text{Na}^+ + \text{K}^+)$ ; (b) main anions:  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  of Lake Pumayum Co. Line AB:  $\text{Ca}^{2+}/\text{Mg}^{2+}=1$

of local soil (Zhang *et al.*, 2004). But compared with river water, the relative proportions of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$  in precipitation increase, especially that of  $\text{Cl}^-$ . For example, the  $\text{Cl}^-$  proportion in anions of Lhase precipitation (7.74%–8.36%) is 400 times of that of JQ1-1(0.02%), but the TDS of the former is only 1/4 of that of the latter. Furthermore, the concentration of  $\text{Cl}^-$  in the former (21.49–21.55  $\mu\text{mol/L}$ ) is 90 times of that of the latter (0.242  $\mu\text{mol/L}$ ). Therefore, two results can be concluded: compared with surface water, precipitation is influenced by sea salt more evidently; the huge hydrochemical difference between the two waters indicates that precipitation has little influence on the ion composition of surface water.

### 3.2.3 Influences of rock weathering on hydrochemistry of lake area

The high value of  $\text{Na}^+/\text{Cl}^-$  excludes the possible influence of salty rocks and evaporites.

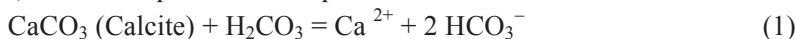
Ternary diagrams of anions and cations have also been used to study the relative importance of different weathering regimes (Figure 4). In Figure 4a, most of the points fall at the left side, namely, far from the  $\text{Na}^+ + \text{K}^+$  apex, showing little contribution from  $\text{Na}^+ + \text{K}^+$  and much contribution from  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  mainly originate from weathering of carbonates and evaporites (such as gypsum) as well as the possible source from the silicate of alkaline earth. Compared with the points of lake water, the points of river water fall farther away from the  $\text{Na}^+ + \text{K}^+$  apex, showing more  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and less  $\text{Na}^+$  and  $\text{K}^+$  (from Table 2, except the two little streams,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  account for more than 60% and 30%, summing up to more than 90%).

The position of lake water points also indicates more  $\text{Mg}^{2+}$  and  $\text{Na}^+$  and less  $\text{Ca}^{2+}$ . In the enclosed lake basin, even both  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  come from dolomite, the molar ration is not more than 1 (Zhang *et al.*, 1995, see eq. (1)). In Figure 4a, compared with most of the rivers samples, the points of lake (in the circle) fall above the line AB ( $\text{Mg}^{2+}/\text{Ca}^{2+}=1$ ), showing the obvious difference between the supplying rivers and the lake. The missing  $\text{Ca}^{2+}$  may be related to the sedimentary process of the lake itself. Because of the intensive evaporation,  $\text{Ca}^{2+}$  is precipitated as carbonate from the water, resulting in the increase of the ratio of  $\text{Mg}^{2+}/\text{Ca}^{2+}$ .

Generally,  $\text{Na}^+$  and  $\text{K}^+$  originate from magmatic rocks or metamorphic rocks, such as some silicate minerals like albite, orthoclase, and mica. The higher concentration of  $\text{Na}^+$  and  $\text{K}^+$  in lake water also results from the evaporation and condensation of lake water.

In Figure 4b, all the points are distributed along the  $\text{HCO}_3^-$  axis, showing insignificant concentration of  $\text{Cl}^-$ . The points of rivers (ellipse I) are distributed on high value end of the  $\text{HCO}_3^-$ , showing the absolutely predominant proportion in the anion composition.  $\text{SO}_4^{2-}$  only occupies 2%–7% of the total anions (Table 2). The points of RDHK, JQHK, central lake area, and the deeper area of JQHK and KQHK (depth more than 1 m) are in ellipse II, located on the lower position of  $\text{HCO}_3^-$  axis, showing decrease of  $\text{HCO}_3^-$  and increase of  $\text{SO}_4^{2-}$  (occupying 20%–35%). The decrease may be related to the precipitation of carbonate. The points of KQHK (depth less than 1 m) are in ellipse III, where  $\text{SO}_4^{2-}$  accounts for 50%–70%.

Generally,  $\text{HCO}_3^-$  is supplied by consuming  $\text{CO}_2$  in atmosphere and soil by means of the incongruent weathering of silicate and by diluting the carbonate in carbonic acid, i.e., congruent weathering (Berner and Berner, 1987).  $\text{SO}_4^{2-}$  is supplied by dissolution weathering of evaporites and oxidation weathering of pyrite (Li, 1988). Carbonate weathering is the major source of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , the main equations are expressed as:



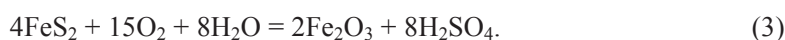
The molar ratios can be deduced:  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^- = 0.5$  or  $\text{Ca}^{2+}/\text{HCO}_3^- = 0.5$  (Zhang *et al.*, 1995). The molar ratio of  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$  of inflows is about 0.5, namely, about 1 in equivalent ratio (Table 3), indicating that the significant process influencing the hydrochemistry of rivers is the carbonate weathering.

**Table 3** Molar ratio  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$  (a) and  $\text{Ca}^{2+}/\text{HCO}_3^-$  (b) of inflow river

Name	JQZW 1-1	JQZW 2-1	JQ 1-1	JQH 1-1	JQH 1-2	KQ 1-1	XSW 1-1	XSW 2-1	XSW 3-1	DQBYW 1-1	RDHW 1-1	RDHW 1-2
a	0.52	0.51	0.49	0.42	0.42	0.50	0.51	0.51	0.49	0.53	0.51	0.51
b	0.34	0.35	0.38	0.12	0.12	0.38	0.34	0.35	0.41	0.26	0.32	0.32

Under the geological background not dominated by the silicate of alkaline earth (Bureau of Geology and Mineral Resources of Tibet Autonomous Region, 1993), the equivalent ratio of  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{TZ}^+ > 0.9$  and  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^- \approx 1$  indicate the carbonate weathering is the main source of the dissolved ions (Sarin *et al.*, 1989; Pandey *et al.*, 1999; Singh and Hasnain, 1999; Singh and Hasnain 2002). In addition, the ratio of  $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+) = 2\text{--}25$ , which is much more than the molar abundance ratio of 1 (Taylor and McLenna, 1985) in the silicates of the upper crust. Therefore, silicate weathering has little influence on the ion composition of this area. The analysis above also means little  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  left for  $\text{SO}_4^{2-}$ , indicating the  $\text{SO}_4^{2-}$  should not be contributed by dissolution of gypsum. Combining with the iron concentration of more than 40 g/kg in lake sediment, the third abundance metal element, it is concluded that the source of  $\text{SO}_4^{2-}$  should come from the oxidation weathering of pyrite.

The equation of chemical weathering of pyrite ( $\text{FeS}_2$ ) in oxidation zone (shallow water area) is expressed as:



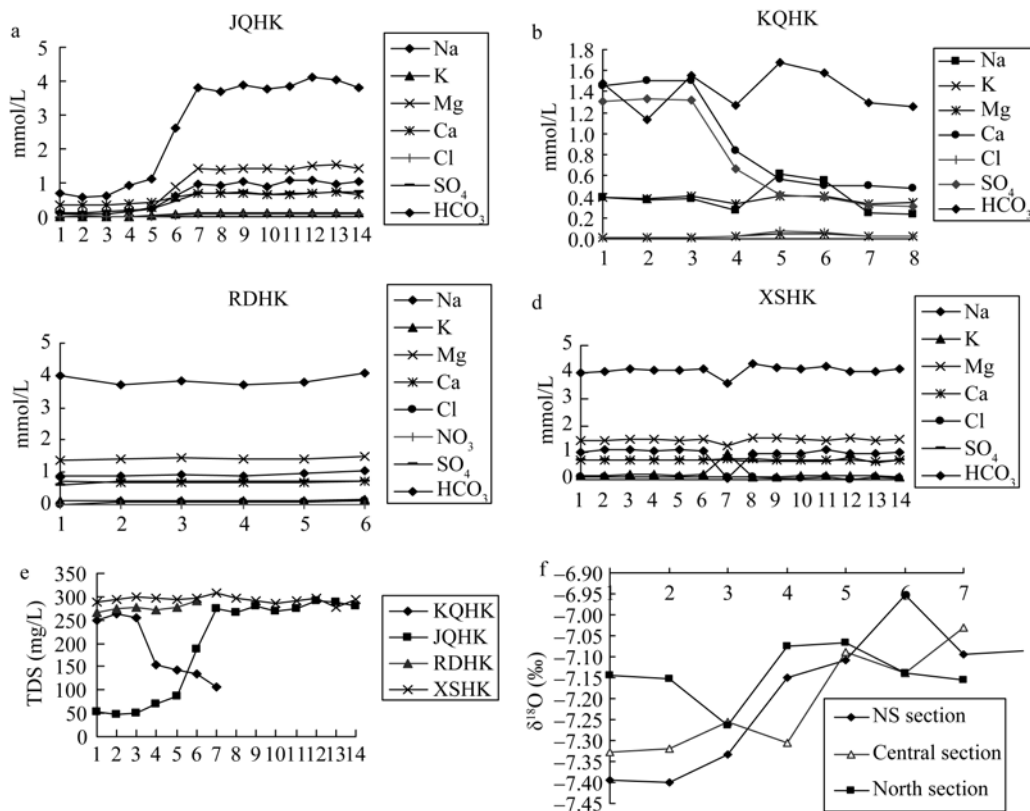


The pH of this lake is 8–10. As the weathering product, the bivalent iron is oxidated to trivalent iron, which can be precipitated into the sediment under the alkalinescent background. Therefore, much iron can be found in sediment and little in water. In Figure 4b, the points in the ellipse III is about the samples in the shallow water area of KQHK, near the north bank. The high value of  $\text{SO}_4^{2-}$  may be resulted from more pyrite distributed on the north bank.

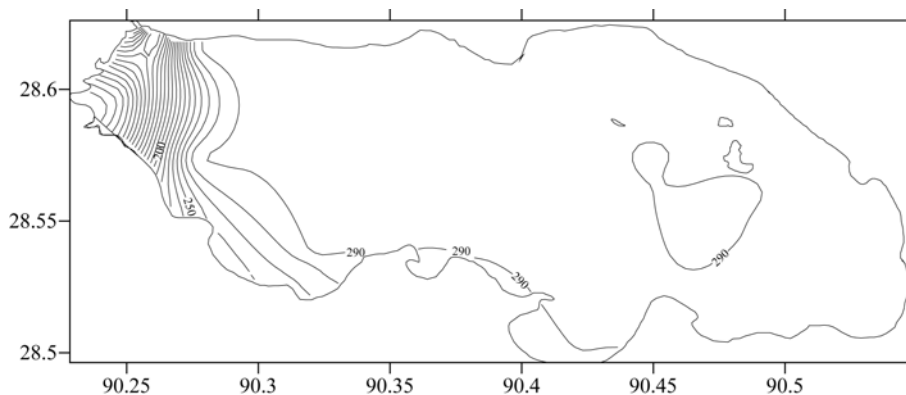
According to above analysis, the main ions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  are dominated by carbonate (calcite and dolomite) weathering. Silicate weathering has less influence on the hydrochemistry and  $\text{SO}_4^{2-}$  is related to the oxidation weathering of pyrite. The dissolution weathering of halite and evaporite is not evident. Concerning to the lake water, besides those relevant processes mentioned above, the hydrochemistry is also influenced by the carbonate sedimentation of the lake itself, which results in the loss of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ .

### 3.3 Spatial distribution of hydrochemistry and oxygen isotope in surface lake water

(1) Spatial distribution of hydrochemistry of lake surface water. Water ion characteristics of the surface water in four lake bays, namely, JQHK, KQHK, RDHK, and XSHK, were analyzed along four transects (see Figure 2) respectively (Figures 5a–5e). The chemistry of water in JQHK and KQHK, into which the Jiaqu River and Kongqu River flows, is characterized by obvious spatial heterogeneity (Figures 5a, 5b, 5e). Along the JQHK transect, the



**Figure 5** Spatial distribution of hydro-parameter of Lake Pumayum Co. x-axis is sample numbers. (a)–(d) show the four survey lines in the lake; (e) indicates the TDS variation in four parts of Lake Pumayum Co (see Figure 2); (f) shows spatial variations of oxygen isotope according to the 3 survey lines (see Figure 2)



**Figure 6** Contour map of total dissolved solids (TDS (mg/L))

concentration of ions and total dissolved solids (TDS) increase in offshore direction. They begin to increase at station 3 (water depth 1.6 m) and increase evidently at station 5 (water depth 2 m) afterwards. Due to the different increasing amplitude of ions, there exist significant changes in the water composition: concentrations of  $Mg^{2+}$  and  $Na^+$  become the first and second predominant ions in cationic constitution unlike inshore water and Jiaqu River water. Whereas at station 7 (water depth 2.8 m), ion chemistry is stable with the TDS less than 300 mg/L (Figures 5a and 5e). In other lake bays, there is no obvious spatial variation (Figures 5c–5e), which indicates the water chemistry has little relationship to the distance to the river mouth. The TDS isoline map (Figure 6) of the lake also shows horizontally heterogenous distribution at the western part of the lake. The spatial variations of water ions indicate that Jiaqu River has more broad influences on ion spatial hydrochemical distribution of lake water.

(2) Spatial distribution of  $\delta^{18}O$  of lake surface water. The surface runoff of Lake Pumayum Co catchment is recharged mainly by ice-snow melting water. In the ocean glaciers area, during the transformation process from ice-snow to melting, and then to river water, the vertical variation gradient of the  $\delta^{18}O$  increases gradually, which is related to the fractionation induced by re-evaporation in the flow of water (Pang, 2006). The  $\delta^{18}O$  of lake water is not the same as it is recharged water. Due to the evaporation, there is considerable enrichment of heavy isotope in the lake water to a certain degree. In the arid area, strong evaporation results in the continuous enrichment of heavy isotope in lake water. Therefore, with the increase of the distance to the inflow point, the  $\delta^{18}O$  increase with the salty degree (Yin, 1988). Thus, the  $\delta^{18}O$  can reflect the influence of different supplying source on lake.

The values of  $\delta^{18}O$  in various types of water take on great difference in this area, namely,  $-20\text{‰}$  (Yin, 2006) in precipitation in rainy season,  $-16.4\text{‰}$  in Jiaqu River and  $-7\text{‰}$  in lake surface water (Figure 5f, see Figure 2 for the transects). The great difference between lake water and river water illuminates the relative enrichment of heavy oxygen isotope results from evaporation on the lake surface. Although the difference is considerably small among inner lake surface water, spatial variation is also evident from the three transects in the central lake area,  $\delta^{18}O$  increases from  $-7.33\text{‰}$  to  $-7.03\text{‰}$ ; and in the lake bay of XSHK,  $\delta^{18}O$  increase from  $-7.41\text{‰}$  to  $-7.09\text{‰}$ . This variation is similar to that of TDS in this lake.

## 4 Conclusions

(1) The chemical type of the lake water was  $Mg^{2+}-Ca^{2+}-HCO_3^- -SO_4^{2+}$ , but the major ions

of the main inflow river were  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ - $\text{HCO}_3^-$ .

(2) Gibbs plot illuminated that the predominant process controlling the hydrochemistry was rock weathering. Ternary plots and ionic ratios not only revealed that water ions origin from the weathering of carbonate, pyrite, and silicate, but show the hydrochemical difference among inflows and lake water. The difference of hydrochemical composition in river mouth has close relationship with the flux of the recharged inflows. The spatial difference is evident in the river mouth of the large river, such as Jiaqu River and Kongqu River. Moreover, the samples in other river mouths and broad lake area were distributed basically in the same area of Gibbs plot and ternary plots, which indicate that those rivers have little influence on the lake. The spatial variation of hydrochemistry and oxygen isotope in lake water further showed the influence of the rivers originated from the glaciers in the south on the lake.

(3) Comparison of chemistry between river water and the lake water at different parts of the lake can help us find that, another evident phenomenon is variation of concentration of  $\text{Ca}^{2+}$  besides the TDS difference. Comparative TDS difference between rivers and lake (54 mg/L in Jiaqu River, 290 mg/L in major part of Lake Pumayum Co) may result from intensive evaporation of this area. During the process of concentration induced by evaporation,  $\text{Ca}^{2+}$  deposited more easily in the form of carbonate owing to its lower solubility than that of magnesium salt in water (Shen, 1986). Therefore, loss of  $\text{Ca}^{2+}$  occurred in the lake. This behavior is consistent with observations of rivers in or near the Tibetan Plateau. In Mansar Lake, located on the southern slope of the Himalayas, the high Mg/Ca ratio during summer compared with the spring is due to preferential extraction of calcium by precipitation (Al-Mikhlafla *et al.*, 2003). Studies on the Ganga–Brahmapu River also revealed that doubling of the Mg/Ca ratio of lowland during their lean flow to peak flow most probably resulted from the preferential removal of calcium by precipitation as carbonate (Handra *et al.*, 1972; Sarin *et al.*, 1989). Therefore, endogenic calcite must be an important feature of sediments in this lake. In addition to the weathering of carbonate, silicate, and pyrite, the depositing process of  $\text{Ca}^{2+}$ , or carbonate deposition in other words, must be another factor influencing the ion composition.

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## References

- AL-Mikhlafla, Das B K, Kaur P, 2003. Water chemistry of Mansar Lake (India): An indication of source area weathering and seasonal variability. *Environmental Geology*, 44(6): 645–653.
- Berner E K, Berner R A, 1987. *The Global Water Cycle*. Prentice-Hall, Englewood Cliffs, 397.
- Bureau of Geology and Mineral Resources of Tibet Autonomous Region, 1993. *Regional Geology of the Tibet Autonomous Region*. Beijing: Geological Publishing House, 142. (in Chinese)
- Chen Jing'an, Wang Guojiang, Huang Ronggui, 2000. Recent climatic changes and the chemical records in

- Chenghai Lake. *Marine Geology and Quaternary Geology*, 20(1): 39–43. (in Chinese)
- Gibbs R J, 1970. Mechanism controlling world water chemistry. *Science*, 170: 1088–1090.
- Gu Zhaoyan, Liu Jiaqi, Yuan Baoyin *et al.*, 1994. Lacustrine authigenic deposition expressive of environment and the sediment record from Siling Co, Xizang (Tibet), China. *Quaternary Sciences*, (2): 162–174. (in Chinese)
- Guan Zhihua, Chen Chuanyou, Qu Yuxiong *et al.*, 1984. The Rivers and Lakes of Tibet. Beijing: Science Press, 141. (in Chinese)
- Handra B K, 1972. Geochemistry of the Ganga River Water. *Indian Geohydrology*, (2): 71–78.
- Hem John D, 1985. Study and interpretation of the chemical characteristics of natural water. Alexandria, VA: Department of the Interior, U.S. Geological Survey, US Water-Supply Paper, 2254.
- Ju Jianting, Zhu Liping, Wang Junbo *et al.*, 2009. Water and sediment chemistry of Lake Pumayum Co, South Tibet, China: Implications for interpreting sediment carbonate. *Journal of Paleolimnology*, doi: 10.1007/s10933-009-9343-6
- Li Bingyuan, Wang Fubao, Zhang Qingsong *et al.*, 1983. Quaternary Geology in Tibet. Beijing: Science Press, 15. (in Chinese)
- Li Xueli, 1988. Hydrogeochemistry. Beijing: Atomic Energy Publishing House, 19. (in Chinese)
- Pandey S K, Singh A K, Hasnain S I, 1999. Weathering and geochemical processes controlling solute acquisition in Ganga Headwater–Bhagirathi River, Garhwal Himalaya, India. *Aquatic Geochemistry*, 5: 357–379.
- Pang Hongxi, He Yuanqing, Lu Aigang *et al.*, 2006. Comparisons of Stable Isotopic Fractionation in Winter and Summer at Baishui Glacier No.1, Mt. Yulong A. *Journal of Geographical Sciences*, 61(5): 501–509. (in Chinese)
- Sarin M M, Krishnaswami S, Dilli K *et al.*, 1989. Major ion chemistry of the Ganga–Brahmaputra river system: Weathering processes and flux to the Bay of Bengal. *Geochim Cosmochim Acta*, 53: 997–1009.
- Shen Zhaoli (ed.), 1986. The Hydro-Geochemistry. Beijing: Gedogy Press, 77–78, 83. (in Chinese)
- Sheng Wenkun, Wang Ninglian, Pu Jianchen, 1996. The hydrochemical characteristics in the Dongkemadi Glacier area, Tanggula Range. *Journal of Glaciology and Geocryology*, 18(3): 235–243. (in Chinese)
- Singh A K, Hasnain S I, 1999. Environmental geochemistry of Damodar River basin–east coast of India. *Environmental Geology*, 37: 124–136.
- Singh A K, Hasnain S I, 2002. Aspects of weathering and solute acquisition processes controlling chemistry of sub-alpine proglacial streams of Garhwal Himalaya, India. *Hydrological Processes*, 16: 835–849.
- Stallard R F, Edmond J M, 1983. Geochemistry of Amazon. 2 The influence of geology and weathering environment on the dissolved load. *Journal of Geophysical Research*, 88: 9671–9688.
- Taylor S R, McLennan S M, 1985. The Continental Crust: Its Composition and Evolution. Oxford: Blackwell.
- Wang Sumin, Dou Hongshen (eds.), 1998. China Lake Records. Beijing: Science Press, 405. (in Chinese)
- Wu Yanhong, Wang Sumin, Xia Weilan *et al.*, 2001. Environmental variation in central Tibetan Plateau in the last 200 years. *Science in China (Series D)*, 44(suppl. 1): 264–268. (in Chinese)
- Yin Changliang, Tian Lide, Yu Wusheng *et al.*, 2006. Variations of stable oxygen isotope in precipitation in the basin of Yamzho Lake. *Journal of Glaciology and Geocryology*, 28(6): 919–924. (in Chinese)
- Yin Guan (ed.), 1988. Isotope Hydrology Geochemistry. Chengdu: Chengdu University of Science and Technology Press, 68–100, 146–147. (in Chinese)
- Zhang Dian, Shi Changxin, Jia La, 2004. A study of chemical properties of rains on the Tibetan Plateau. *Journal of Environmental Sciences*, 24(3): 555–557.
- Zhang J, Huang WW, Letolle R *et al.*, 1995. Major element chemistry of the Huanghe (Yellow River), China: Weathering processes and chemical fluxes. *Journal of Hydrology*, 168: 173–203.
- Zhao Huabiao, Yao Tandong, Xu Baiqing, 2006. Hydrological and hydrochemical features of Kartamak Glacier Area in Muztag Ata. *Journal of Glaciology and Geocryology*, 28(2): 269–275. (in Chinese)
- Zhu Liping, Chen Ling, Li Bingyuan *et al.*, 2002. Environmental changes reflected by the lake sediments of the South Hongshan Lake, Northwest Tibet. *Science in China (Series D)*, 45: 430–439.
- Zhu Liping, Ju Jianting, Wang Junbo *et al.*, 2006. Environmental changes recorded in core sediments from the Pumoyum Co Lake of the Tibetan Plateau during the initial stage of the last deglacial period. *Quaternary Sciences*, 26(5): 772–780. (in Chinese)
- Zhu Liping, Wang Junbo, Chen Ling *et al.*, 2004. 20000-year environmental change reflected by multidisciplinary lake sediments in Chen Co, southern Tibet. *Acta Geographica Sinica*, 59(4): 514–524. (in Chinese)