Comparison of surface water chemistry and weathering effects of two lake basins in the Changtang Nature Reserve, China

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Received 27 February 2015

Revised 02 March 2015

Accepted 03 March 2015

Abstract: The geochemistry of natural waters in the Changtang Nature Reserve, northern Tibet, can help us understand the geology of catchments, and provide additional insight in surface processes that influence water chemistry such as rock weathering on the Qinghai-Tibet Plateau. However, severe natural conditions are responsible for a lack of scientific data for this area. This study represents the first investigation of the chemical composition of surface waters and weathering effects in two lake basins in the reserve (Lake Dogaicoring Qiangco and Lake Longwei Co). The results indicate that total dissolved solids (TDS) in the two lakes are significantly higher than in other gauged lakes on the Qinghai-Tibet Plateau, reaching 20-40 g/L, and that TDS of the tectonic lake (Lake Dogaicoring Qiangco) is significantly higher than that of the barrier lake (Lake Longwei Co). Na^+ and Cl^- are the dominant ions in the lake waters as well as in the glacier-fed lake inflows, with chemical compositions mainly affected by halite weathering. In contrast, ion contents of inflowing rivers fed by nearby runoff are lower and concentrations of dominant ions are not significant. Evaporite, silicate, and carbonate weathering has relatively equal effects on these rivers. Due to their limited scope, small streams near the lakes are less affected by carbonate than by silicate weathering.

Key words: Surface water geochemistry; rock weathering; Changtang Nature Reserve; Qinghai-Tibet Plateau

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Introduction

Ion contents and chemical compositions of surface waters are affected by a number of factors, including climate, geology, and human activities. The study of water geochemistry reveals the pattern and linkage between climate, weathering, and tectonic impacts (Brennan and Lowenstein, 2002). The Qinghai-Tibet Plateau, often called the “Third Pole”, is extremely sensitive to global climate change. In particular, the water chemistry of many of the plateau’s lakes is affected by changes in the surrounding basin hydrology (Mitamura et al., 2003). In recent decades, research on the surface water chemistry of the Qinghai-Tibet Plateau has mostly focused on areas with convenient access and significant impacts of human activities, such as the Qaidam Basin (Tan et al., 2011), Qinghai Lake (Xiao et al., 2012; Xu et al., 2010), and river source regions (Noh et al., 2009; Qin et al., 2006; Wu et al., 2005, 2008) in the Qinghai Province, China. Investigations and analyses of large lakes and rivers located in central and southern Tibet are equally abundant, such as studies of Lake Nam Co (Wang et al., 2009; Zhang et al., 2008), Lake Yamzhog Yumco (Sun et al., 2013; Zhang et al., 2012), Lake Mapam Yumco (Wang et al., 2013), and the Yarlung Tsangpo River Basin (Guilmette et al., 2009; Hren et al., 2007). These studies have greatly enhanced the knowledge about the chemical characteristics and evolution of lake and river waters on the Qinghai-Tibet Plateau. For example, Ju et al. (2010) showed that Ca^{2+} , Mg^{2+} , and HCO_3^- were the dominant ions in Lake Pumayum Co and its inflows, which are located in southern Tibet. Spatial variation in the chemical composition of the lake water was shown to depend on the characteristics of its inflows. Wang et al. (2010a) analyzed 76 samples of lake water and 69 samples of river water flowing into Lake Nam Co on the central Tibetan Plateau, and found that Na^+ , Ca^{2+} , and HCO_3^- were the main ions, accounting for 60.6%-93.4% of total dissolved solids (TDS). Evaporative crystallization was shown to control the chemical composition of Lake Nam Co, and rock weathering, especially of carbonates and silicates, appeared to be the primary source

of ions for its inflows. However, basic scientific understanding of lake basins and their water chemistry in the higher altitude regions of northern Tibet is still limited owing to geographical conditions.

The Changtang Nature Reserve in northern Tibet is the second largest natural reserve in China and provides protection for the local alpine ecosystem and many types of rare animals. This region is centered in the world's second largest inland lake area (Changtang Plateau), which includes 441 closed lakes with surface areas over 1 km². The total lake area in this region is 9652 km² (Li et al., 2013), comprising 40% of the total lake area in Tibet. In contrast to the low latitude areas in Tibet, the reserve is characterized by extreme natural conditions and difficulty of access, which has resulted in a lack of information on its water chemistry. A comparative study of the chemical composition of two lake basins in this region and associated controlling mechanisms can not only reveal differences and linkages among different types of surface water, but also provide additional insight into the chemical effects of natural processes such as rock weathering. In addition, this research can provide important background information for global change studies of extreme environments.

Rock composition and weathering are the primary factors determining river water composition (Drever, 1994). In this study, end-member and ion comparison analyses were applied to determine the effects of rock weathering on surface water chemistry. Subsequently, a forward model was used to calculate the contribution of ions from weathering of three typical rock types. From this, the spatial variations of surface water chemistry in two lake basins as well as the correlation between the chemical characteristics of waters and the geologic setting were determined.

1 Materials and methods

1.1 Study area

The Changtang Plateau covers an area of over 700,000 km² and includes the raised plateau as well as surrounding mountains, including the Tanggula, Kunlun, and Hoh Xil Mountains. The Changtang Natural Reserve is located at the junction of Ngari and Nagqu Prefectures, has an average altitude of more than 5000 m, and covers an area of 298,000 km².

The average annual precipitation is 100-200 mm, with an average annual temperature of -6 to -4°C. The area is dominated by a network of small seasonal rivers (Chen and Guan, 1989). Both Lake Dogaicoring Qiangco (DQ) and Lake Longwei Co (LW) are located in the region, with a distance of about 182 km between them (**Fig. 1**).

Lake DQ is a lake in the southern piedmont of Kangzhagri Mountain, which is the highest peak in the Hoh Xil mountain range. The lake is located at 35°19'N and 89°15'E at an elevation of 4787 m. The surface area of Lake DQ has been expanding over the past two decades, and reached about 300 km² in 2010. The maximum depth of the lake is about 28 m. The lake water is mainly recharged by runoff from snow and glacier melt from Glacier Kangzhagri (elevation 6305 m) and Glacier Rola Kangri (elevation 6036 m), the latter being the highest peak in the Rola Kangri mountains, located southwest of the lake. In addition, the lake is fed by a number of small streams formed by springs surrounding the lake.

Lake LW is located in a volcanic area, and given its physical setting, is a barrier lake. The lake is located at 33°52'N and 88°18'E at an elevation of 4942 m. The surface area of Lake LW is about 44 km², with a maximum depth of about 10 m. The largest river flowing into the lake is the Heishi River, which originates from the Glacier Nadi Kangri (elevation 6004 m). The glacier forms the highest peak in the Nadi Kangri volcanic cluster, which is located about 40 km southwest of the lake. Small streams formed by springs surrounding the lake provide some additional inflow.

In the study area, sparse grassland and barren land are the two dominant land use types, and alpine steppe soil comprises 92.3% of the total area (Bureau of Land Management of Tibet Autonomous Region, 1994). Rocks are primarily Pleistocene and Pliocene in age (Tian and Ding, 2006; Yang et al., 2000), with widely distributed shale, limestone, and siltstone (Bureau of Geology and Mineral Resources of Tibet Autonomous Region, 1993). In addition, silicates and coal-bearing clastics exist around Lake DQ and frost weathering occurs in the slope sediments at the bottom of the stratum. In contrast, the Lake LW basin is composed of volcanics, such as trachyandesite, as well as some sedimentary rocks, such as gypsum, with clastics forming the base of the stratum.

1.2 Sampling and analytical methods

With access limited by road and environmental conditions, the study area could be reached only in winter when a large number of small seasonal rivers were frozen. Therefore, the sampling period for Lakes DQ and LW ranged from 24 October to 7 November 2012. Wang et al. (2010a) have shown that spatial and vertical variations in ion composition in one lake are relatively small between depths of 0-30 m. Therefore, surface water samples from the two lakes were collected at a depth of 30-40 cm. Owing to terrain limitations, samples from Lake DQ basin were collected from the southern end of the lake, while those from Lake LW basin were collected from the eastern and western sides of the lake (**Fig. 1**). In total, 38 samples were collected, including three types of surface water samples (lake, river, and small stream). Two rivers were sampled in each lake basin. In the Lake DQ basin, the Wuquan River (DA) is fed by runoff from Rola Kangri peak, and an unnamed river (DB) also originates in the Rola Kangri mountains. In the Lake LW basin, an unnamed river (LA) originates in the volcanic cluster about 10 km west of the lake, whereas the Heishi River (LB) is fed by runoff from Nadi Kangri peak. A total of nine samples from small streams surrounding Lake DQ (DS) and three samples from small streams around Lake LW (LS) were collected (**Table 1**).

Water samples collected were stored in pre-cleaned HDPE bottles and kept frozen. Major cation (K^+ , Na^+ , Ca^{2+} , Mg^{2+} and Si) concentrations were measured using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (PerkinElmer Corporation, USA). Anion concentrations (SO_4^{2-} , Cl^- , and NO_3^-) were determined by High Performance Liquid Chromatography (LC-10ADvp) (Shimadzu Corporation, Japan). The procedural blanks were determined in parallel with the sample treatment using identical procedures. Each calibration curve was assessed by analyses of quality control standards before, during and after the analyses of samples. In general, the precision is $\pm 2\%$ for cations and $\pm 5\%$ for anions. Because surface water CO_3^{2-} concentrations are low in northern Tibet (Wang and Dou, 1998), alkalinity is represented by HCO_3^- . Using ionic charge balance (Ju et

al., 2010; Wu et al., 2008), the equivalent of HCO_3^- was calculated to determine TDS.

2 Results and discussion

2.1 General characteristics and controlling factors of water chemistry

Both DQ and LW lakes are salt-water lakes with TDS reaching 23.4-31.4 g/L, which is much higher than other gauged lakes on the Qinghai-Tibet Plateau, such as Qinghai Lake, Lake Zhari Namco, and Lake Tangra Yumco (**Table 2**). Additionally, the TDS in samples from Lake DQ is 1.34 times higher than in samples from Lake LW. The TDS levels of the DQ and LW inflows, including rivers and small streams, range from 0.37 to 0.91 g/L, with the exception of LB, which is 3.03 g/L (**Table 3**). This TDS level is also higher than that of water from other rivers on the plateau (0.1-0.3 g/L on average) (Sun et al., 2013). The TDS of the rivers flowing into Lake LW are 2.4 times higher than those of rivers flowing into Lake DQ. The TDS of small streams flowing into the two lakes show less spatial variation than the rivers. The TDS of the streams around Lake DQ are 1.6 times higher than those of streams flowing into Lake LW. Therefore, the ion contents of the lakes are not only impacted by the chemical composition of the inflows, but also by other factors such as the period for which a lake had been formed.

Based on analyses of global natural surface waters, Gibbs (1970) found that chemical composition was controlled by three factors: evaporation and crystallization, rock weathering, and precipitation. The relationship between TDS and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ or TDS and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ was used to determine the controlling factor that dominates in a given body of water. The two lakes in this study have both high TDS and a high ratio of $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$, indicating that they are mainly controlled by evaporation and crystallization. Data from river and small stream samples cluster in the middle of the Gibbs plot (**Fig. 2**), with a relatively higher TDS than the global average for rivers (0.07-0.13 g/L) (Chen et al., 2002; Meybeck and Helmer, 1989). This indicates that the chemical composition of inflowing waters is mostly affected by rock weathering, which is similar to the control mechanism of other rivers on the Qinghai-Tibet Plateau (Ju et al., 2010; Wang et al., 2010a). Among the different

inflows, the ratios of $\text{Cl}^-/(\text{Cl}^-+\text{HCO}_3^-)$ can be divided into three categories: (1) higher than 0.7 (DA and LB); (2) from 0.3 to 0.6 (DB and DS); and (3) approximately 0.2 (LA and most of LS). Accordingly, the ion composition of inflows is largely controlled by rock type and intensity of weathering.

2.2 Major ion compositions

The coefficient of variance (CV) of each ion content in different samples from the same lake water ranges from 0.1 to 0.2. The average CV of nine ions in rivers DA, DB, LA, and LB is 0.29, 0.37, 0.25, and 0.16, respectively (**Table 3**). This indicates that ion composition is relatively consistent in the same river water. In contrast, the average CV of nine ions in streams DS and LS is 1.03 and 0.75, respectively. Despite being among samples from the same basin, the CV of each ion in small stream waters is higher, because the stream samples were collected from different sites around the lakes. This indicates a spatial heterogeneity in the chemical composition of those streams. Given this variation, the average ion content was used when the chemical characteristics were compared between the two lake waters, and single values were applied when the water chemistry of inflowing rivers and streams was analyzed.

2.2.1 Lake waters

A Piper diagram was used to represent the chemistry of surface waters (**Fig. 3**). The diagram shows relative amounts of different components, and indicates variations in chemical characteristics and controlling factors (Li and Zhang, 2008; Ryu et al., 2008). The two lake water samples cluster near the Na^+ and Cl^- end-members, indicating that both lakes belong to the chemical type Na-Cl, typical of salt lake waters (Kilham, 1990; Xu et al., 2010). Na^+ and Cl^- in Lake DQ represent 41% and 40% of the molar equivalent of ion content, respectively, while in Lake LW, those elements represent 47% and 40%, respectively (**Table 2**). Other cations are also present in Lakes DQ and LW, with $\text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+}$, which together represent 7% (DQ) and 4.3% (LW) of the molar equivalent of ion content. The ion composition shows no difference from that of Lake Nam Co, but the ions are present at much

higher concentrations (Wang et al., 2009). The cation content appears to be much higher in Lake DQ than it is in Lake LW, and Na^+ , Mg^{2+} , K^+ , and Ca^{2+} are 1.2, 2.2, 2.3, and 1.8 times higher, respectively. This implies that Lake DQ formed prior to Lake LW as a result of its location in the basin, and a longer period of evaporation and crystallization has resulted in the accumulation of a greater quantity of ions. In contrast, Lake LW (a barrier lake) was formed by volcanic activity and has a much lower concentration of ions. Both HCO_3^- and SO_4^{2-} show major differences between the two lakes. In Lake DQ, which is similar to Lake Nam Co (Wang et al., 2009), HCO_3^- and SO_4^{2-} make up 12.3% and 0.6% of total ion content (molar equivalent), respectively, and show a much larger difference than in Lake LW. However, HCO_3^- and SO_4^{2-} have similar weight percentages in Lake LW (5% and 4.2% of the molar equivalent of ion content, respectively) to those in Lake Qinghai and Lake Yamzhog Yumco (Sun et al., 2013; Xiao et al., 2012). SO_4^{2-} in Lake LW is 6.4 times higher than that in Lake DQ, whereas HCO_3^- is only one quarter of that in Lake DQ. This suggests that the terrain surrounding Lake LW and its inflows contains a greater amount of sulfate, while the area around Lake DQ has more carbonate. In addition, NO_3^- and Si are extremely low in both lakes. However, while there is no NO_3^- in Lake LW, there is 2.5 times more Si than in Lake DQ. The low NO_3^- in the study area can be attributed to very little human activity such as agriculture and stock farming in the area. Therefore, the only possible contributor would be sedimentation.

2.2.2 Inflowing river waters

There is a large difference in the ion content between the two lake basins (**Table 3**). In rivers DA and DB (two rivers flowing into Lake DQ), the absolute difference in ion content is 0.1-5.3 mmol/L. In particular, concentrations of K^+ , Na^+ , Ca^{2+} , Cl^- , and SO_4^{2-} in DA are greater than those in DB, with Ca^{2+} being 3.5 times higher and the rest about 1.5-2.7 times more on average. In contrast, Mg^{2+} , HCO_3^- , and Si in DB are higher than in DA by factors of 1.5, 1.2, and 1.4, respectively. The difference in ion content between rivers LA and LB (the two rivers flowing into Lake LW) is larger than that for rivers DA and DB. Concentrations of Na^+ and Cl^- are 35 and 78 times greater, respectively, in LB than in LA, whereas the other

ions are generally 0.9-2.9 mmol/l higher, with an average of 1.5 mmol/l.

The ion composition of the rivers appears to be affected by a variety of environmental conditions (**Table 4**). In the Piper diagram, water samples from rivers DA and DB have very similar ratios of $\text{Na}^+ - \text{K}^+$ and SO_4^{2-} , accounting for about 55% and 20% of the total equivalent of cations and anions, respectively (**Fig. 3**). However, there is an obvious difference in the equivalent ratio of total cations of Ca^{2+} and Mg^{2+} in river DA (28.5% and 11.8%, respectively) compared to river DB (14.7% and 30.6%, respectively). Cl^- makes up about 60% of all anions and HCO_3^- and SO_4^{2-} contents are similar in river DA, while in DB, HCO_3^- is the dominant anion at 2 times more than SO_4^{2-} , making up 42% of all anions. The water chemical type of river DA is Na-Ca-Cl- HCO_3 , while river DB is Na-Mg- HCO_3 -Cl.

Water samples from rivers LA and LB show a much different distribution in the Piper diagram. In river LA, Ca^{2+} and SO_4^{2-} are the dominant ions, making up 47.9% of total cations and 57.8% of total anions, while Mg^{2+} and HCO_3^- make up 34.4% of total ions. In contrast, river LB samples cluster near the Na^+ and Cl^- end-members, with equivalent cation and anion percentages of 78.5% and 74.7%, respectively. In addition, in river LB, the proportion of other ions is less than 10%, except for the ratio of SO_4^{2-} to total anions, which is 14.2%. The water chemical type of river LA is Ca-Mg- SO_4 - HCO_3 while LB is Na-Cl- SO_4 .

These results show that the origin of a river may be one of factors controlling the chemical compositions of the water. For instance, rivers DA and LB originate from glaciers that are located far from the lake, whereas rivers LA and DB are fed by nearby runoff. In general, rivers that flow greater distances contain more ions, and in particular, those originating from glaciers may be affected mostly by the melting processes. On the other hand, rivers that originate from other runoff may be more strongly affected by the geologic setting.

2.2.3 Inflowing small stream waters

On average, the ion content of streams flowing into Lake DQ (DS) is two times higher than those in streams around Lake LW (LS), with ion concentrations of 13.8 and 9.5 mmol/l, respectively (**Table 3**). There is a large difference in SO_4^{2-} and Si concentrations between DS and LS. Additionally, ion compositions vary widely, even among streams flowing into a

single lake (**Table 5**). For instance, the stream southwest of Lake DQ (DS4) and the stream to the south of Lake LW (LS4) contain more ions than any other stream waters (except Si in LS4). In particular, Na^+ is over 10 times higher than in the other streams.

The distribution of data from streams around the same lake is relatively concentrated in the Piper diagram. There are few outliers, which indicate that the variation in chemical composition between different streams flowing into one lake is not as significant as that within rivers (**Fig. 3**). The cation characteristics of DS were: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$, with just two anion characteristics of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. In addition, the concentrations of Mg^{2+} and SO_4^{2-} in DS make up about 20% each of the total cations and anions. Around Lake LW, the LS water chemistry is consistent with Na-Ca-Mg- HCO_3 - SO_4 , with the exception of LS4, which is Na-Cl. In addition, the concentrations of Mg^{2+} and HCO_3^- in LS make up about 20% and 50% of total cations and anions, respectively. As a result of little runoff, the chemical composition of small stream waters is mainly affected by the surrounding geology.

2.3 Effect of chemical weathering on inflow components

Gaillardet et al. (1999) studied 60 large rivers and established relationships between surface water chemistry and rock types. Their findings indicated that the contribution of different rocks to surface water chemistry can be represented by the relationships between $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+$, and between $\text{Ca}^{2+}/\text{Na}^+$ and $\text{HCO}_3^-/\text{Na}^+$, which has been widely used in the studies of weathering effects (Gao et al., 2009; Leybourne and Goodfellow, 2010). Under natural conditions, the main sources of K^+ and Na^+ are evaporite and silicate weathering. On the other hand, Ca^{2+} and Mg^{2+} may be derived from evaporites, silicates, or carbonates. HCO_3^- originates mostly from evaporite and silicate weathering, whereas Cl^- and SO_4^{2-} are derived mostly from weathering and dissolution of evaporites (Li et al., 2009; Meybeck, 1987).

Linear correlations exist between $\text{Mg}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$, and between $\text{HCO}_3^-/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ for inflows into Lakes DQ and LW ($r^2 = 0.92$ and 0.83 , respectively). Rivers DA,

DB, and the streams have a molar ratio that places them in the center of the diagram (**Fig. 4**). The $\text{Mg}^{2+}/\text{Na}^+$ ratio for river DA is approximately 0.1, showing the influence of evaporites. However, river DB is mainly influenced by silicate weathering, and the data points are clustered near the silicate end-member. Data points from streams are dispersed, which is likely the result of very little runoff contribution. However, silicate weathering appears to be the main factor controlling the chemical composition of these stream waters. The three ratios of $\text{Mg}^{2+}/\text{Na}^+$, $\text{Ca}^{2+}/\text{Na}^+$, and $\text{HCO}_3^-/\text{Na}^+$ for river LA are close to or greater than 1.0. It can be inferred that carbonate weathering has a significant impact on the water chemistry of this river. On the other hand, these three molar ratios for river LB are less than 0.1, which indicates that the river chemistry is significantly affected by evaporites.

Because the ratios of Na^+ to Cl^- are almost 1.0 for the inflows into Lake DQ (DA, DB, and DS) and river LB (**Fig. 5a**), halite weathering appears to have a more significant effect than silicate weathering on these bodies of water (Xu et al., 2010). In contrast, the ratios of Na^+ to Cl^- for rivers LA and LS are greater than 1.0, which indicates that both evaporite and silicate weathering contribute to those waters.

Because silicate and carbonate weathering releases less Ca^{2+} and Mg^{2+} than Na^+ and K^+ (Sarin et al., 1989), the $(\text{Na}^+ + \text{K}^+)$ concentrations of the samples are much higher than the $(\text{Ca}^{2+} + \text{Mg}^{2+})$ concentrations (**Fig. 5b**). Differences in sample distributions demonstrate the effects of differential chemical weathering. Samples from rivers DA, DB, and the streams fall on or slightly below (DA) a line of $(\text{Na}^+ + \text{K}^+) = (\text{Ca}^{2+} + \text{Mg}^{2+})$, indicating that the ion contribution from carbonate weathering almost compensates for the lower amount of Ca^{2+} and Mg^{2+} relative to Na^+ and K^+ released during silicate weathering. This suggests stronger carbonate weathering compared to silicate weathering. Unlike in any other samples, $(\text{Ca}^{2+} + \text{Mg}^{2+})$ is higher than $(\text{Na}^+ + \text{K}^+)$ in river LA, which shows that carbonate weathering has a greater influence on the ion composition of the water (Ju et al., 2010). However, halite weathering greatly impacts river LB, as shown by $(\text{Na}^+ + \text{K}^+)$ being four times higher than $(\text{Ca}^{2+} + \text{Mg}^{2+})$ in those samples.

In order to investigate the impact of sulfate weathering on river chemical composition, it

is helpful to compare the correlation between $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and HCO_3^- , and that between $(\text{Ca}^{2+}+\text{Mg}^{2+})$ and $(\text{HCO}_3^-+\text{SO}_4^{2-})$ (**Fig. 5c** and **d**). Samples from rivers DB, DS, and LS mainly cluster on a line of $(\text{Ca}^{2+}+\text{Mg}^{2+}) = \text{HCO}_3^-$, which indicates a minor contribution of sulfate weathering to the water ion composition. The primary sources of Ca^{2+} and Mg^{2+} for these waters are carbonate and silicate weathering. In contrast, all data points from DA are located on the line of $(\text{Ca}^{2+}+\text{Mg}^{2+}) = (\text{HCO}_3^-+\text{SO}_4^{2-})$, which shows that all Ca^{2+} and Mg^{2+} is derived from carbonate and sulfate (Moquet et al., 2011). It is possible that the primary source of SO_4^{2-} for river DA was gypsum dissolution and weathering. In river LA, $(\text{Ca}^{2+}+\text{Mg}^{2+})$ falls between HCO_3^- and $(\text{HCO}_3^-+\text{SO}_4^{2-})$, which indicates that a portion of the SO_4^{2-} is derived from pyrite oxidation and weathering. Data for LB are scattered, but $(\text{Ca}^{2+}+\text{Mg}^{2+})$ is higher than HCO_3^- . This illustrates that sulfate weathering influences the river's composition, but the source of SO_4^{2-} appears to be spatially heterogeneous.

2.4 Quantification of rock weathering sources

A mass balance forward model (Galy and France-Lanord, 1999) was applied to estimate ion contributions to the two lakes and their inflows from three types of rock weathering. The study area is far from the oceans and generally arid with an average annual precipitation of less than 200 mm, so we assumed that the influence of sea salt and rainfall on water chemistry can be ignored (Ju et al., 2008; Zhang et al., 1995). In addition, the study area is located in remote northern Tibet, so anthropogenic inputs to the dissolved load were also ignored. Therefore, the mass balance equation for the waters in the study area can be written as:

$$[\text{X}]_{\text{water}} = [\text{X}]_{\text{carbonate}} + [\text{X}]_{\text{silicate}} + [\text{X}]_{\text{evaporite}} \quad (1)$$

The forward model was expressed as a series of budget equations based on two assumptions. First, Cl^- in the waters was assumed to come from halite. Second, SO_4^{2-} was assumed to be derived from gypsum and pyrite at a 1:1 ratio. Based on these assumptions, the budget equations are as follows:

$$[\text{Cl}]_{\text{water}} = [\text{Cl}]_{\text{evaporite}} \quad (2)$$

$$[\text{SO}_4]_{\text{water}} = [\text{SO}_4]_{\text{sulfate}} = [\text{SO}_4]_{\text{Gypsum}} + [\text{SO}_4]_{\text{Pyrite}} \quad (3)$$

$$[\text{Na}]_{\text{water}} = [\text{Na}]_{\text{silicate}} + [\text{Cl}]_{\text{evaporite}} \quad (4)$$

$$[\text{K}]_{\text{water}} = [\text{K}]_{\text{silicate}} \quad (5)$$

$$[\text{Ca}]_{\text{water}} = [\text{Ca}]_{\text{carbonate}} + [\text{Ca}]_{\text{silicate}} + [\text{SO}_4]_{\text{Gypsum}} \quad (6)$$

$$[\text{Mg}]_{\text{water}} = [\text{Mg}]_{\text{carbonate}} + [\text{Mg}]_{\text{silicate}} \quad (7)$$

Because it is difficult to estimate the contribution of Ca^{2+} and Mg^{2+} from carbonates and silicates, the ratio between Ca^{2+} and Mg^{2+} versus Na^+ was assumed to be constant during silicate weathering. Research on rock weathering on the Qinghai-Tibet Plateau indicated that the composition of plagioclase was generally taken as representative to determine the contribution of silicate weathering to the waters (Hren et al., 2007; Noh et al., 2009; Wu et al., 2008). In plagioclase, $\text{Ca}^{2+}/\text{Na}^+ = 0.5 \pm 0.25$ and $\text{Mg}^{2+}/\text{Na}^+ = 0.2 \pm 0.1$. Therefore, 0.5 and 0.2 were used to represent the ratios of $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+$ during silicate weathering, respectively. Eqs. (6) and (7) were then revised as:

$$[\text{Ca}]_{\text{water}} = [\text{Ca}]_{\text{carbonate}} + 0.5 \times [\text{Na}]_{\text{silicate}} + [\text{SO}_4]_{\text{Gypsum}} \quad (8)$$

$$[\text{Mg}]_{\text{water}} = [\text{Mg}]_{\text{carbonate}} + 0.2 \times [\text{Na}]_{\text{silicate}} \quad (9)$$

Thus, the total ion contribution (meq/l) from weathering of three rock types can be calculated from Eqs. (10)-(12):

$$[\text{X}]_{\text{evaporite}} = [\text{Na}]_{\text{evaporite}} + [\text{Ca}]_{\text{evaporite}} \quad (10)$$

$$[\text{X}]_{\text{silicate}} = [\text{Na}]_{\text{silicate}} + [\text{K}]_{\text{silicate}} + 2 \times [\text{Ca}]_{\text{silicate}} + 2 \times [\text{Mg}]_{\text{silicate}} \quad (11)$$

$$[\text{X}]_{\text{carbonate}} = 2 \times [\text{Ca}]_{\text{carbonate}} + 2 \times [\text{Mg}]_{\text{carbonate}} \quad (12)$$

In river DA, evaporite weathering contributes 66% to the total concentration of cations at about 10 meq/L, followed by carbonate weathering, which accounts for 31.8% (**Table 6, Fig. 6**). The effect of silicate weathering can largely be ignored. However, the effects of the three rock types on river DB's water chemistry are relatively similar, with an average cation concentration of 2-4 meq/L, and cation contributions from evaporites, silicates, and

carbonates of 43.5%, 34.9%, and 21.6%, respectively. In addition, the water chemistry of streams around Lake DQ is predominantly controlled by silicate and evaporite weathering, with cation concentrations of 2.7-4.1 meq/L.

The cation contribution to river LB is significantly higher than to river LA, indicating that the area of the LB river basin is likely far greater than that of the LA river basin. In river LB, the contribution from evaporite weathering accounts for 70.8% of total cations with an average cation concentration of about 40 meq/l. In contrast, the chemical composition of river LA is the result of the combined effects from evaporite and carbonate weathering, both of which contribute 2.3-2.6 meq/L of cations to the water. The contribution of sulfate weathering and dissolution to the cations in the two rivers flowing into Lake LW is 1.3 meq/L on average, which is 2.6 times greater than that of the rivers flowing into Lake DQ. In addition, the water chemistry of the streams around Lake LW is predominantly controlled by evaporite and silicate weathering, with cation concentrations of 2.5-3.3 meq/L.

In a closed lake, ions accumulate gradually with the evaporation of water. The lake water can become supersaturated and ions will precipitate out in a certain order based on their different saturation states. For instance, Ca^{2+} precipitates easily, whereas Na^+ can accumulate to much higher levels before precipitating. Therefore, the chemical composition of lake water is controlled by the composition of its inflows as well as by evaporation intensity and formation time of the lake itself. The halite in Lakes DQ and LW was produced by evaporation, resulting in cation concentrations of 363.55 and 275.45 meq/L, which account for 69% and 61% of the total concentration, respectively. Other chemical components are mainly derived from inflow. Owing to the more intense silicate weathering around Lake LW, the water has a cation concentration of 40 meq/L more than that of Lake DQ. In contrast, the contribution of inflows affected by carbonate weathering to Lake LW is less than 10 meq/L; conversely, the contribution to Lake DQ is about eight times that to LW. Because of the spatial distribution of sulfate minerals in the two lake basins, sulfate contribution to Lake LW is far greater than to Lake DQ.

3 Conclusions

Owing to the combined effects of climate and geological setting, Lakes DQ and LW, located in the Changtang Nature Reserve, both have high salinity. Ion contents of waters in these two lake basins are significantly higher than those in other gauged lake basins on the Qinghai-Tibet Plateau. This may result from the integrated impacts of higher latitude, higher altitude, and less water storage. The TDS of Lake DQ is significantly higher than that of Lake LW. This difference can be attributed to the fact that Lake DQ is much older than Lake LW; Lake DQ is a tectonic lake located in the remote Hoh Xil region, whereas Lake LW is a barrier lake formed by more recent volcanic activity. Both lakes are impacted by evaporation and crystallization, but there are considerable differences in anion concentrations between these two bodies of water due to the chemistry of their inflows. It is highly possible that more sulfate minerals are present in the LB river basin; as a result, river LB contains more SO_4^{2-} than any of the other rivers in the area, which in turn has led to much more SO_4^{2-} in Lake LW than in Lake DQ.

Rivers DA and LB, which originate from glaciers, show significant differences in salinity, chemical composition, and rock weathering mechanisms compared to rivers DB and LA, which are fed by other nearby runoff. Rivers DA and LB both have high concentrations of TDS. Chemical compositions of both rivers are affected by halite weathering, resulting in cation concentrations of 8.46 and 36.1 meq/L, respectively. As a result, the equivalent percentages of Na^+ and Cl^- in the river waters are about 60% and 80% of total cations and anions, respectively. However, in rivers DB and LA, these ions do not contribute significantly to the total dissolved load. In addition, evaporite, silicate, and carbonate weathering resulted in similar ion contributions to both rivers, with differences less than 1.5 meq/L. Small stream samples collected from surrounding areas showed a higher consistency in ion compositions than rivers. However, these small streams are affected more by carbonate than silicate weathering. Overall, the chemical characteristics of rivers DB, LA, and the inflowing stream waters indicate that their composition is in direct relationship with variations in geology.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 41190080, 41371058, and 41201035), the National Science Foundation of China (No. 2012FY111400) and the Chinese Academy of Sciences Strategic Leading Science and Technology Projects (No. XDB05030400). Additionally, we also thank Dr. Y. Wang, Dr. X. Hu, and Dr. Q. Ma of the Institute of Tibetan Plateau Research, Chinese Academy of Sciences, for participation in the field investigations.

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List of tables

Table 1 Sampling type and number in Lake Dogaicoring Qiangco (DQ) and Lake Longwei Co (LW) basins

Table 2 Comparison of chemical components for lakes in the Qinghai-Tibet Plateau

Table 3 Average content and coefficient of variation (CV) value of the chemical components in inflowing waters

Table 4 Chemical compositions of the dissolved loads in different inflowing rivers (equivalent)

Table 5 Chemical compositions of the dissolved loads in different inflowing streams (equivalent)

Table 6 Cation contributions of rock weathering for lakes and their inflows in the study area

List of figures

Fig. 1 Location of the study area, showing the sample locations, elevation and landuse distribution.

Fig. 2 Gibbs plot showing TDS versus ratio of $\text{Cl}^-/(\text{Cl}^-+\text{HCO}_3^-)$ with the equivalent unit. In Gibbs diagram, Lower TDS (0.01 g/L) and higher ratio of $\text{Cl}^-/(\text{Cl}^-+\text{HCO}_3^-)$ (close to 1) reflects the dominance of precipitation; medium TDS (0.07-0.3 g/L) and lower ratio (lower than 1) points the control of rock weathering, and high TDS and higher ratio (close to 1) indicates the influence of evaporation and crystallization (Chen, 1987).

Fig. 3 Piper plot of major ions in lakes and their inflowing waters in the study area with the equivalent unit. In Piper diagram, the position of each point was a weighted group of three kinds of ions, the relative contents of which ultimately should be equal to 100% when get them together.

Fig. 4 End-member mixing plots with the ionic molar ratios of the inflow waters in the study area. (a) shows the relation between Mg^{2+} and Ca^{2+} and (b) shows that between HCO_3^- and

Ca^{2+} of different inflowing waters, respectively. End-member mixing plot was a logarithmic diagram, using ratios of Mg^{2+} or HCO_3^- and Ca^{2+} which have been normalized by Na^+ .

Fig. 5 Equivalent comparison between different ions of the inflowing waters in the study area, showing (a) Na^+ vs. Cl^- , (b) $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs. Na^++K^+ , (c) $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs. HCO_3^- and (d) $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs. $\text{HCO}_3^-+\text{SO}_4^{2-}$.

Fig. 6 Comparison of cation contributions of three kinds of rock weathering for waters in the study area. Evaporites contribution includes that from Halite and Sulfate.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

List of Tables

Table 1 Sampling type and number in Lake Dogaicoring Qiangco (DQ) and Lake Longwei Co (LW) basins

	Sample group	Sampling type	Sampling site	Sampling range	Sample number (Sam.#)
Lake DQ	DQ	Lake water	South side of Lake	6 km	9 (D1-D9)
	DA	River water	Wuquan River	8 km	7 (DA1-DA7)
	DB	River water	An unnamed river	12 km	3 (DB1-DB3)
	DS	Stream water	Streams on south bank of Lake	40 km	6 (DS1-DS6)
Lake LW	LW	Lake water	East side of Lake	2 km	3 (L1-L3)
	LA	River water	An unnamed river	8 km	3 (LA1-LA3)
	LB	River water	Heishi River	12 km	3 (LB1-LB3)
	LS	Stream water	Streams around Lake		4 (LS1-LS4)

Table 2 Comparison of chemical components for lakes in the Qinghai-Tibet Plateau

Lake	TDS (g/L)	K ⁺ (mmol /L)	Na ⁺ (mmol /L)	Ca ²⁺ (mmol/ L)	Mg ²⁺ (mmol /L)	Cl ⁻ (mmol /L)	SO ₄ ²⁻ (mmol /L)	HCO ₃ ⁻ (mmol /L)	Reference
DQ	31.4	24.2	386.9	8.95	31.4	363.6	5.44	115.2	This study
LW	23.4	10.7	326.5	4.84	14.5	275.5	34.7	29.3	This study
QH	18.1	4.24	191.8	0.57	33.4	226.4	29.5	29.2	Xu et al., 2010
TY	11.1	-	-	-	-	-	-	-	Wang et al., 2010b
ZN	7.74	-	-	-	-	-	-	-	Wang et al., 2010b
NC	1.2	0.89	13.9	0.18	3.28	3.65	2.15	13.8	Wang et al., 2010a
YY	1.28	0.46	12.3	0.18	7.85	2.31	7.25	9.74	Sun et al., 2013
PC	0.1	0.45		1.12	1.03	0.05	0.81	1.75	Ju et al., 2010
LC	0.49	0.52	7.65	0.32	4.48	1.94	1.12	13.3	Wang et al., 2013
MY	0.46	0.15	2.13	0.67	1.20	0.39	0.31	4.93	Wang et al., 2013

QH: Lake Qinghai; TY: Lake Tangra Yumco; ZN: Lake Zhari Namco; NC: Lake Nam Co; YY: Lake Yamzhog Yumco; PC: Lake Pumayum Co; LC: Lake La'ang Co; MY: Lake Mapam Yumco. “-” represent that the ion concentration of these lakes are not reported in the reference.

Table 3 Average content and coefficient of variation (CV) value of the chemical components in inflowing waters

Gro up	K ⁺ (mmo l/L)	Na ⁺ (mmo l/L)	Ca ²⁺ (mmo l/L)	Mg ²⁺ (mmo l/L)	Cl ⁻ (mmo l/L)	HCO ₃ ⁻ (mmol/ L)	SO ₄ ²⁻ (mmol/ L)	NO ₃ ⁻ (mmol/ L)	Si (mmol/ L)	TDS (g/L)
Inflow of Lake DQ										
DA	0.29 (0.4)	8.13 (0.3)	1.94 (0.2)	0.82 (0.3)	8.46 (0.4)	2.86 (0.2)	1.29 (0.3)	0.11 (0.3)	0.15 (0.2)	0.91 (0.3)
DB	0.19 (0.4)	4.39 (0.5)	0.55 (0.2)	1.23 (0.3)	3.14 (0.5)	3.33 (0.3)	0.83 (0.3)	0.08 (0.6)	0.2 (0.2)	0.57 (0.4)
DS	0.21 (1.4)	4.32 (1)	1.03 (0.5)	0.7 (0.6)	2.81 (0.7)	0.89 (1)	3.38 (1)	0.05 (1.7)	0.36 (1.5)	0.58 (0.9)
Inflow of Lake LW										
LA	0.07 (0.3)	1.09 (0.4)	1.54 (0.2)	1.11 (0.2)	0.47 (0.3)	2.22 (0.2)	1.89 (0.2)	0.04 (0.3)	0.11 (0.2)	0.46 (0.2)
LB	1.32 (0.1)	38.1 (0.1)	2.4 (0.1)	2.16 (0.1)	36.5 (0.2)	5.11 (0.2)	3.35 (0.6)	0.15 (0.1)	0.26 (0.1)	3.03 (0)
LS	0.11 (0.9)	3.55 (1.2)	0.54 (0.3)	0.37 (0.3)	2.55 (1.5)	0.68 (0.5)	1.56 (0.3)	0.04 (0.9)	0.07 (0.8)	0.37 (0.8)

Table 4 Chemical compositions of the dissolved loads in different inflowing rivers (equivalent)

Group	Sam.#	K ⁺ (meq)	Na ⁺ (meq)	Ca ²⁺ (meq)	Mg ²⁺ (meq)	Cl ⁻ (meq)	HCO ₃ ⁻ (meq)	SO ₄ ²⁻ (meq)	NO ₃ ⁻ (meq)	Si (meq)
Inflowing river of Lake DQ										
DA	DA1	0.59	13.15	4.95	2.53	14.25	3.46	3.42	0.13	0.17
	DA2	0.24	7.03	4.22	1.43	7.23	3.19	2.44	0.14	0.16
	DA3	0.27	8.30	3.67	1.68	8.47	2.95	2.47	0.11	0.15
	DA4	0.14	4.16	2.17	0.89	4.30	1.61	1.42	0.03	0.09
	DA5	0.33	10.20	4.52	2.06	10.63	2.97	3.45	0.12	0.18
	DA6	0.24	7.06	3.83	1.44	6.96	3.17	2.40	0.11	0.16
	DA7	0.24	6.99	3.82	1.46	7.35	2.67	2.44	0.10	0.15
DB	DB1	0.13	3.83	0.84	2.63	2.55	2.98	1.89	0.07	0.19
	DB2	0.29	7.00	1.45	3.40	5.24	4.71	2.16	0.13	0.25
	DB3	0.16	2.32	1.01	1.38	1.61	2.30	0.95	0.03	0.15
Inflowing river of Lake LW										
LA	LA1	0.10	1.69	3.66	2.83	0.65	2.69	4.93	0.06	0.13
	LA2	0.07	1.05	2.28	1.88	0.46	1.97	2.84	0.03	0.12
	LA3	0.04	0.55	3.30	1.96	0.30	1.99	3.56	0.03	0.09
LB	LB1	1.41	40.48	5.19	4.58	45.81	4.46	1.13	0.13	0.23
	LB2	1.36	39.12	4.24	4.68	35.50	4.09	9.60	0.15	0.26
	LB3	1.20	34.70	4.96	3.70	28.22	6.77	9.40	0.17	0.29

Table 5 Chemical compositions of the dissolved loads in different inflowing streams (equivalent)

Group	Sam.#	K ⁺ (meq)	Na ⁺ (meq)	Ca ²⁺ (meq)	Mg ²⁺ (meq)	Cl ⁻ (meq)	HCO ₃ ⁻ (meq)	SO ₄ ²⁻ (meq)	NO ₃ ⁻ (meq)	Si (meq)
Inflowing stream of Lake DQ										
DS	DS1	0.08	2.82	1.77	1.53	1.73	3.26	1.19	0.00	0.45
	DS2	0.05	1.03	1.05	0.73	0.77	1.53	0.55	0.01	0.21
	DS3	0.10	4.47	1.80	1.63	5.05	1.13	1.78	0.01	0.51
	DS4	0.86	13.77	4.49	3.18	6.06	10.74	5.46	0.21	1.72
	DS5	0.05	1.61	1.75	0.66	1.54	2.12	0.40	0.01	0.29
	DS6	0.12	2.19	1.50	0.68	1.69	1.50	1.28	0.02	0.31
Inflowing stream of Lake LW										
LS	LS1	0.07	1.61	0.76	0.70	0.42	1.48	1.24	0.10	0.24
	LS2	0.05	0.98	1.25	0.62	0.30	1.30	1.30	0.03	0.21
	LS3	0.03	0.77	0.75	0.56	0.46	1.07	0.59	0.03	0.15
	LS4	0.28	10.84	1.59	1.05	9.02	2.40	2.28	0.00	0.89

Table 6 Cation contributions of rock weathering for lakes and their inflows in the study area

Group	Evaporites			Silicates	Carbonates
	Halite	Sulfate	Sum		
	meq	meq	meq	meq	meq
Lake					
DQ	363.55	2.72	369.00	92.43	66.49
LW	275.45	17.37	310.19	133.17	8.53
Inflows of Lake DQ					
DA	8.46	0.64	9.75	0.33	4.70
DB	3.14	0.42	3.97	3.19	1.97
DS	2.81	0.44	3.70	4.07	1.45
Inflow of Lake LW					
LA	0.47	0.94	2.36	1.57	2.54
LB	36.51	1.68	39.86	9.40	7.00
LS	2.55	0.34	3.23	2.51	0.37

First investigation of water ion chemistry in no-man's land

Comparison of chemical composition

Quantification of rock weathering sources

Mass Balance Forward Model

$$[X]_{\text{water}} = [X]_{\text{carbonate}} + [X]_{\text{silicate}} + [X]_{\text{evaporite}}$$