



# Chemical weathering processes in the Yalong River draining the eastern Tibetan Plateau, China



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## ABSTRACT

To better understand chemical weathering and controlling processes in the Yalong River of the eastern Tibetan Plateau, this study presents major ion concentrations and stable isotopes of the dissolved loads. The isotopic compositions ( $\delta^{13}\text{C}$ -DIC,  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ - $\text{SO}_4$ ) of the dissolved loads are very useful to quantify solute sources and define the carbon budget related with chemical weathering in riverine systems. The isotopic composition of sulphate demonstrates that most of the sulphate is derived from sulphide oxidation, particularly in the upper reach of the Yalong River. The correlations between  $\delta^{13}\text{C}$ -DIC, water chemistry and isotopes of sulphate, suggest that the carbon dynamics are mainly affected by carbonate weathering by sulphuric acid and equilibration processes. Approximately 13% of the dissolved inorganic carbon in the Yalong River originates from carbonate weathering by strong acid. The  $\text{CO}_2$  consumption rates are estimated to be  $2.8 \times 10^5 \text{ mol/km}^2/\text{yr}$  and  $0.9 \times 10^5 \text{ mol/km}^2/\text{yr}$  via carbonate and silicate weathering in the Yalong River, respectively. In this study, the influence of sulphide oxidation and metamorphic  $\text{CO}_2$  on the carbon budget is estimated for the Yalong River draining the eastern Tibetan Plateau.

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## 1. Introduction

Rock weathering and the burial of organic carbon are the two main sinks of atmospheric  $\text{CO}_2$  in the global carbon cycle and thus affect Earth's climate on short to geological timescales (Bernier et al., 1983; France-Lanord and Derry, 1997; Ludwig et al., 1998; Gaillardet et al., 1999; Cole et al., 2007). The consumption of atmospheric  $\text{CO}_2$  via silicate weathering would regulate the global  $\text{CO}_2$  level and climate at geological time scales ( $10^6$  year) due to the subsequent  $\text{CO}_2$  sequestration as carbonate in the ocean (Bernier et al., 1983). According to the "tectonics-weathering-climate" hypothesis, the Himalayan uplift would have been responsible for the global cooling and  $\text{CO}_2$  drawdown during the Cenozoic (Raymo and Ruddiman, 1992). However, the influence of rock weathering on the evolution of long-term climate requires more accurate and systematic researches due to uncertainties in the chemical weathering fluxes and complexity of the factors that control these fluxes at the watershed scale (Gaillardet et al., 1999; West et al., 2005; Tipper et al., 2006; Calmels et al., 2007; Gaillardet and Galy, 2008; Noh et al., 2009). Thus, the carbon budget in the river systems should be evaluated more carefully for accurate global carbon cycle.

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The water chemistry and rock weathering in Himalayan and Tibetan rivers have drawn extensive attention (Galy and France-Lanord, 1999; Dalai et al., 2002; Jacobson et al., 2002; Singh et al., 2005; Wu et al., 2005, 2008; Tipper et al., 2006; Hren et al., 2007; Moon et al., 2007; Noh et al., 2009). Several studies have demonstrated the complexity of carbon dynamics in the rivers and the various processes controlling rock weathering as well as sources of the dissolved inorganic carbon in the Himalaya region. It was reported that sulphuric acid should act as an important weathering agent in the Ganges–Brahmaputra (Galy and France-Lanord, 1999) and the Indus (Karim and Veizer, 2000). Recent studies have shown significant quantities of metamorphic  $\text{CO}_2$  were released during the tectonic uplift of the Himalayas, based on data from water chemistry and  $\delta^{13}\text{C}$  of dissolved inorganic carbon (Evans et al., 2008; Becker et al., 2008). However, the chemical budget influenced by sulphuric acid and metamorphic  $\text{CO}_2$  in the eastern Tibetan Plateau rivers are not well known (Wu et al., 2005, 2008; Qin et al., 2006; Moon et al., 2007; Noh et al., 2009). The carbon budget and dynamics should be updated to better understand the chemical weathering process and carbon cycle in the riverine system of the Tibetan Plateau.

In the present study, we focus on the carbon dynamics and rock weathering in the Yalong River draining the eastern Tibetan Plateau, SW China, using water chemistry and isotopic compositions of dissolved inorganic carbon and sulphate. The main objectives

of this study are to identify the sources of solutes, to evaluate the contribution to rock weathering and carbon budget caused by sulphide oxidation and metamorphic CO<sub>2</sub>, and so estimate silicate weathering and CO<sub>2</sub> consumption rates in the Yalong River.

## 2. Materials and methods

### 2.1. Characteristics of the investigated basin

The Yalong River basin is located in the eastern Tibetan Plateau, Southwest China, between 26°32' and 33°58'N latitude and 96°52' to 102°48'E longitude. The Yalong River, one of the largest tributaries of the Changjiang River, originates from the Bayan Har Mountains in the southern Qinghai Province at an elevation of nearly 5000 m. The River has a basin area of  $1.28 \times 10^5$  km<sup>2</sup> with a mainstream river length of over 1571 km. The mean annual water discharge is 1914 m<sup>3</sup>/s, with annually exports on average  $2.55 \times 10^{10}$  kg/yr as suspended particulate matter. About 75% of the total water discharge occurs during the wet season from June to October (Zhu, 2007; Feng et al., 2008). The major tributaries of the Yalong River are the Xianshui River, Qingda River, Liqiu River, Litang River, Jiulong River and Anning River (Fig. 1).

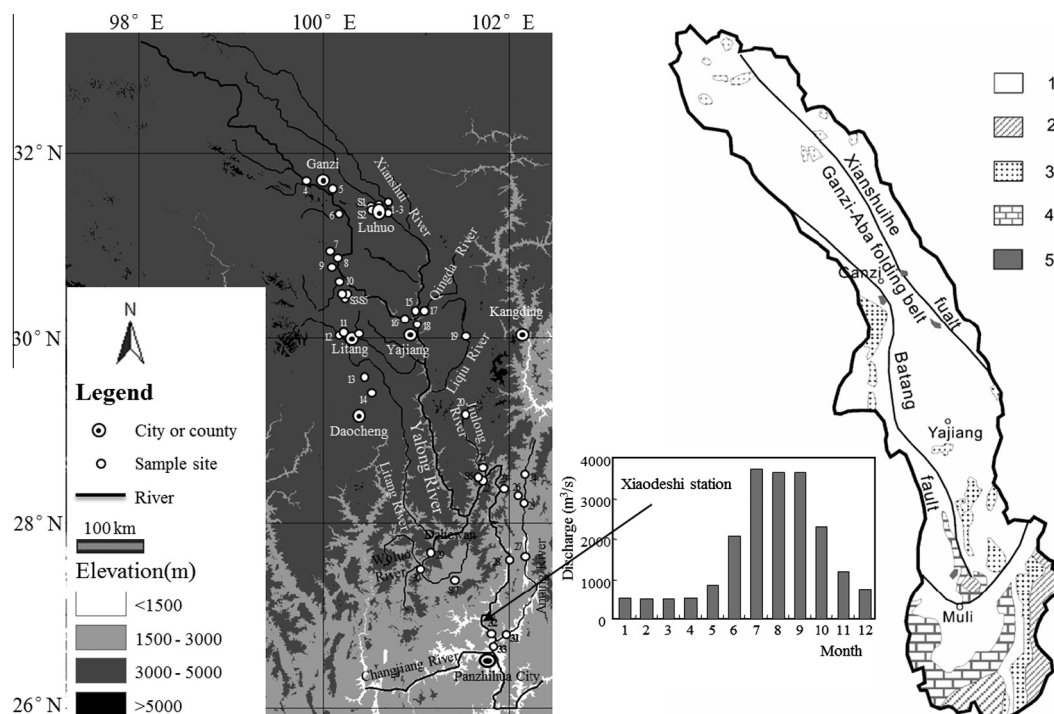
The upper, middle, and lower reaches of the river are geographically divided by Ganzi and Dahewan. The landscape exhibits a plateau strath terrace for the upper main channel and deep gorges for the middle and lower reaches of the Yalong River (Zhu, 2007). The upper and middle reaches of the Yalong River are tectonically situated in the Ganzi-Aba folding belt, with to the Xianshuihe fault and the Batang fault, in the studied area. Triassic sediments including low grade metamorphic rocks outcrop in the upper and middle reaches, which are dominantly sandstone rocks intercalated with sparse granitoid intrusive rocks, Permian carbonate, shale and minor ophiolitic melanges. The areas in the lower reaches are of exposed Palaeozoic carbonates and low-grade metamorphic rocks with minor basalt, gneiss, schist, granite and conglomerate based

on geological survey (Bureau of Geology Mineral Resources of Sichuan Province, 1991).

A seasonal monsoonal climate dominates a wide area of the Yalong River basin and controls the temporal and spatial distribution of precipitation. A cold climate associated with less abundant rainfall dominated the headwater of the basin. The mean annual rainfall varies from 500 to 800 mm in the upper reach, from 1000 to 1800 mm in the middle reach and from 900 to 1300 mm in the lower reach. The runoff of the Yalong River primarily originates from precipitation, snow melting and groundwater. About 90% of the annual precipitation occurs from May to October. The grassland covers approximately 68% of the catchment, and forest land covers approximately 20% of the catchment (Yu et al., 2008). The population density and cultivated land ratio are very low in the Yalong River basin except the suburb of the Panzhuhua City (2.4 million inhabitants) and the Anning plain located in the lower reach. The cultivated land is mainly distributed in the Anning plain at the eastern part of the basin.

### 2.2. Sampling and analytical techniques

Water samples were collected in August 2008 and February of 2010, corresponding to the high flow season and the low flow season, respectively. Temperature, electrical conductivity and pH of the water samples were measured in the field. Alkalinity was determined by HCl titration. Water samples were filtered through 0.45 μm cellulose-acetate filter paper into a series of bottles for analysis. Major cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>) and Si concentrations were measured by ICP-OES with a precision better than 5%. Anions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>) were determined by ionic chromatography Dionex 90 with a precision of 5%. The concentrations of dissolved organic carbon (DOC) were analysed as CO<sub>2</sub> by catalytic combustion (Elemental high TOC II + N, Germany) after water acidification with HCl to remove all inorganic carbon. The values of partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and calcite saturation index (SIc)



**Fig. 1.** Topographic map with sampling site and simplified geology at the Yalong River. Mean monthly discharge at monitoring station refer to Cen et al. (2012) (No. 32). Keys: 1. Mesozoic sediments including low-grade metamorphic rocks; 2. High-grade metamorphic rocks; 3. Granites; 4. Carbonate rocks with clastic rocks; 5. Ophiolitic melanges.

were calculated by equilibrium equations at the given temperature and the thermodynamic constants (Clark and Fritz, 1997).

Oxygen isotopes of water were determined in a Micromass IsoPrime mass spectrometer coupled to an automated line based on the equilibration between H<sub>2</sub>O and CO<sub>2</sub> gas.  $\delta^{18}\text{O}\text{-H}_2\text{O}$  has a precision of 0.2‰. For isotopic analysis of sulphate, the dissolved sulphate was precipitated as BaSO<sub>4</sub> by adding excess BaCl<sub>2</sub> solution after the water was acidified to a pH value of about 3. This precipitation was filtered, washed and dried for isotopic analysis. S and O isotope ratios of sulphate were determined using the elemental analysis-isotope ratio mass spectrometry (EA-IRMS) method, and reported in the  $\delta$  notation relative to the Vienna Canyon Diablo Troilite (V-CDT) and Vienna Standard Mean Ocean Water (V-SMOW) in permil, respectively. The analytical precision for  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of NBS127 and samples was generally better than 0.2‰ and 0.5‰, respectively.

For determination of the  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC), water samples were collected in polyethylene bottles with air-tight caps. Using a modification of the method described by Atekwana and Krishnamurthy (1998), 15-ml aliquots of the water samples were injected by syringe into glass bottles that were pre-filled with 1 ml 85% phosphoric acid and magnetic stir bars. For  $\delta^{13}\text{C}$  analysis of particulate inorganic carbon (PIC) and organic carbon (POC) in the suspended particulate matter (SPM), about 2000 ml water was filtered through pre-washed cellulose acetate filters. The particulate matter on the filter was put into the glass bottles and reacted with the phosphoric acid after vacuum extraction for the analysis of  $\delta^{13}\text{C}\text{-PIC}$ . The particulate inorganic carbon on the filter was removed by adding 1 N HCl. The POC was then transferred into a tube and combusted at 850 °C with CuO and Cu to convert it into CO<sub>2</sub>. The CO<sub>2</sub> was then extracted and purified after cryogenic removal of H<sub>2</sub>O using a liquid nitrogen–ethanol trap. Finally, the CO<sub>2</sub> was transferred cryogenically into a tube for isotope measurement. The carbon isotope ratios of the carbon species were measured using a Finnigan MAT 252 mass spectrometer and reported using the  $\delta$  notation relative to the Vienna Pee Dee Belemnite (V-PDB) in permil. Routine  $\delta^{13}\text{C}$  measurements have a precision of 0.1‰. The results showed that the differences of the duplicated samples generally were less than 0.1‰.

### 3. Results

#### 3.1. Major ions in the water

The major parameters and chemical compositions of the river water are presented in Supplementary Table 1. The pH of the water varies from 7.3 to 8.6, with a mean value of  $8.1 \pm 0.3$ . The water temperature variations range from 9.2 °C to 20.5 °C during the high flow season. The chemical compositions for the Yalong River water are highly variable, with the total dissolved solids (TDS = Ca + Mg + Na + K + Cl + HCO<sub>3</sub> + SO<sub>4</sub> + SiO<sub>2</sub>) ranging from 17 to 346 mg/l. The range of TDS values in the mainstream is from 174 to 275 mg/l during the high flow season and from 214 to 294 mg/l during the low flow season. As indicated by Fig. 2, the water chemistry at a given sampling site, is characterised by a higher TDS value during the low flow season compared with the high flow season. The TDS values of the mainstream in the Yalong River decrease from the upper reach to the lower reach because of the contribution from many tributaries in the middle reach of the Yalong River displaying low TDS values. The TDS values at the mouth of the Yalong River are 175 mg/l during the high flow season and 214 mg/l during the low flow season, respectively.

The total cationic charges ( $\text{TZ}^+ = 2^*\text{Ca} + 2^*\text{Mg} + \text{Na} + \text{K}$ ) are highly variable ranging from 225  $\mu\text{eq/l}$  to 3974  $\mu\text{eq/l}$ . As indicated by Fig. 3, Ca<sup>2+</sup> and Mg<sup>2+</sup> are the dominant cations in the river water,

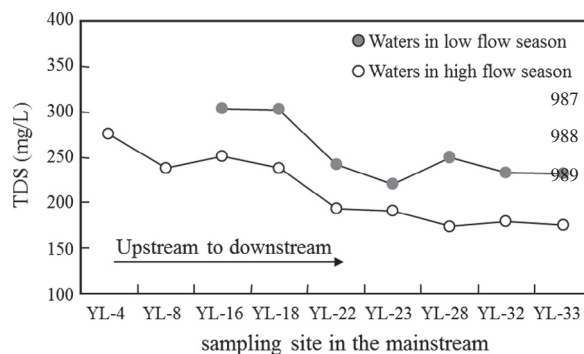


Fig. 2. Variation of the total dissolved solid (TDS) of main channel from upstream to downstream in the Yalong River.

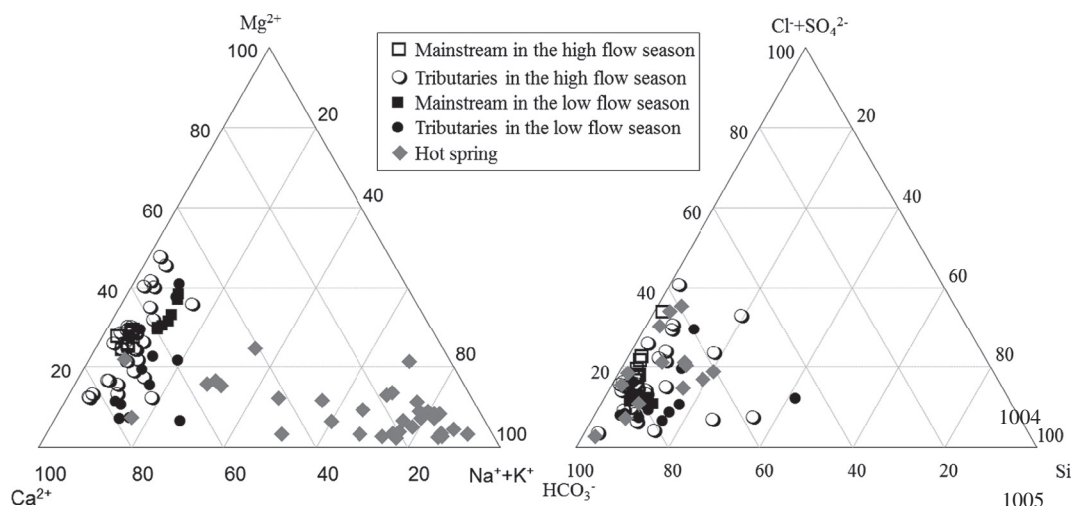
accounting for 73–97% of the total cationic budget. The concentration of Ca<sup>2+</sup> ranges from 78 to 1489  $\mu\text{mol/l}$  with a mean value of 647  $\mu\text{mol/l}$ . The traditional ternary diagrams of the major ions show that more than 60% of the cation is Ca<sup>2+</sup> in most samples from the Yalong River, especially in the high flow season. The following is Mg<sup>2+</sup> with the concentration ranging from 14 to 951  $\mu\text{mol/l}$  with a mean value of 317  $\mu\text{mol/l}$ . The concentrations of Na<sup>+</sup> and K<sup>+</sup> are relatively low. The Na<sup>+</sup> contents ranged from 20 to 462  $\mu\text{mol/l}$  with a mean value of 156  $\mu\text{mol/l}$ . Only small K<sup>+</sup> contents were observed in the river waters with a range of 5–65  $\mu\text{mol/l}$ .

The dominated anions are HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in the river water, which gradually decrease from upstream to downstream. HCO<sub>3</sub><sup>-</sup> has a range of 140–3931  $\mu\text{mol/l}$  with a mean value of 1866  $\mu\text{mol/l}$  in the Yalong River, contributing approximately 58–96% (average: 82%) of the total anion budget and well balanced by Ca<sup>2+</sup> ( $R^2 = 0.86$ , not shown). SO<sub>4</sub><sup>2-</sup> is the second most abundant anion in the river water, with the concentration ranging from 5 to 699  $\mu\text{mol/l}$ . The upper reach has high SO<sub>4</sub><sup>2-</sup> concentration, such as water (No. 4) at Ganzi having a value of 647  $\mu\text{mol/l}$  in the high flow season with the highest SO<sub>4</sub>/HCO<sub>3</sub> ratio of 0.52. The equivalent ratios of SO<sub>4</sub>/HCO<sub>3</sub> range from 0.02 to 0.71, with a mean value of  $0.18 \pm 0.14$ . SO<sub>4</sub> represents approximately 2–41% of the anion charge in mainstream waters in the high flow season and 7–22% of the anion charge in the low flow season. Additionally, the Cl concentration ranges from 0.5 to 283  $\mu\text{mol/l}$  with a mean value of 43  $\mu\text{mol/l}$ . The NO<sub>3</sub> content in most of the samples is lower than 10  $\mu\text{mol/l}$ , which is insignificant with respect to the total anion contribution.

The rain water is characterised by low TDS and major ions contents. The major ions decreased in the order Ca > SO<sub>4</sub> > Mg ~ K > Na > Cl in rain waters. The Cl content in the two analysed rain waters is about 1  $\mu\text{mol/l}$ , which is similar with the lowest value in river water (Nos. 9 and 13). Hot spring water (No. 11) collected near Litang is characterised by high TDS and major ions contents. The chemical composition of the hot spring water is dominated by Na (32.2 mmol/l) for the cations and HCO<sub>3</sub> (39.3 mmol/l) for the anions.

#### 3.2. Isotopic compositions of sulphate

The isotopic compositions of sulphate are highly variable within the entire basin. In the river water, the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of sulphate range from -14‰ to 12‰ with a mean value of  $1.4 \pm 5.3\%$ , and from -12.6‰ to 8.1‰ with a mean value of  $-2.8 \pm 5.1\%$ , respectively. The  $\delta^{34}\text{S}\text{-SO}_4^{2-}$  values of samples from main channel increase from upstream to downstream, from -7.4‰ to 1.4‰ in the high flow season and from 0.2‰ to 2.4‰ in the low flow season, respectively. With the exception of water of No. 4



**Fig. 3.** Ternary plots of cations and anions in the Yalong River. Data are in  $\mu\text{eq/l}$ . Chemical data of hot spring from previous studies (Zhang and Hu, 2000; Gao et al., 2004) except No. 11.

characterised by the lowest  $\delta^{34}\text{S}$  value ( $-7.4\text{‰}$ ), the water samples collected in the main channel show a narrow range of  $\delta^{34}\text{S}$  values primarily from  $0\text{‰}$  to  $2\text{‰}$ . The S and O isotopic compositions of sulphate for the hot spring water are  $9.3\text{‰}$  and  $-2.7\text{‰}$ , respectively. The  $\delta^{34}\text{S}$  values in this study are in agreement with those in the Indus River (Karim and Veizer, 2000), the Minjiang River (Yoon et al., 2008), the Marsyandi River (Turchyn et al., 2013) and the Mackenzie River (Calmels et al., 2007). The sulphate is generally enriched in heavy  $^{18}\text{O}$  isotopes relative to those in the Marsyandi River (Turchyn et al., 2013) and has larger variable range of  $\delta^{18}\text{O}$  values compared with other studies showing limited data in the Himalayas rivers (Karim and Veizer, 2000; Yoon et al., 2008).

### 3.3. Riverine carbon species and isotopes

The saturation state index of calcite (Sic) and the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) can be useful to understand carbonate precipitation and capacity of mineral dissolution (Clark and Fritz, 1997). The  $p\text{CO}_2$  values for the water samples range from  $10^{-4.7}$  to  $10^{-2.5}$  (atm), with a median value of  $10^{-3.2}$  (atm). The Sic values are generally close to zero indicating that most of the water samples are near to equilibrium with respect to calcite. DIC is the sum of the aqueous carbon dioxide ( $\text{CO}_2(\text{aq})$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions. In this study,  $\text{HCO}_3^-$  contributed approximately 99% DIC to the river water after calculation.

The carbon isotopic compositions ( $\delta^{13}\text{C}$ ) of DIC in the river waters vary from  $-12.2\text{‰}$  to  $0.9\text{‰}$ , with a mean value of  $-7.1 \pm 2.6\text{‰}$  during the high flow season and  $-4.6 \pm 2.2\text{‰}$  during the low flow season. The  $\delta^{13}\text{C}$ -DIC values measured in the Yalong River mainstream during the high flow season (from  $-7.6\text{‰}$  to  $-4.8\text{‰}$ ) are generally lower than those measured during the low flow season ( $-5.0\text{‰}$  to  $-3.0\text{‰}$ ) resulting in a seasonal variation of  $\delta^{13}\text{C}$ -DIC of about 1–3‰. The lowest  $\delta^{13}\text{C}$ -DIC values were found in the Anning River and a small sub-tributary near the Panzhuhua City.  $\delta^{13}\text{C}$ -DIC has a similar range of variation with those measured in riverine systems of the Himalaya, e.g. the Ganga–Brahmaputra River system (Galy and France-Lanord, 1999) and the Indus River system (Karim and Veizer, 2000), but are usually higher than those measured values for rivers draining the Deccan Traps (Das et al., 2005) and the Brahmaputra river draining India and Bangladesh (Singh et al., 2005) impacted by basalt weathering. However, the measured values in this study are lower than those in some

Himalayan rivers strongly impacted by hot springs (Becker et al., 2008; Evans et al., 2008).

The POC contents in the suspended particulate matter are generally lower than 1%. The SPM in the mainstream (No. 28) near the mouth of the Yalong River has organic carbon content of 0.8%. The  $\delta^{13}\text{C}$  values of POC have a narrow range from  $-25.4\text{‰}$  to  $-21.9\text{‰}$  with a mean value of  $-24.4 \pm 1\text{‰}$ . The PIC contents of the suspended particulate matter collected in the Yalong River mainstream waters are approximately 1%. The  $\delta^{13}\text{C}$  values of the PIC have also a narrow range from  $-3.4\text{‰}$  to  $-1.0\text{‰}$ .

## 4. Discussion

### 4.1. Sulphate sources

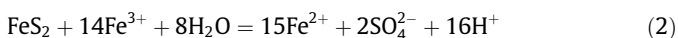
The dual-isotope approach ( $\delta^{34}\text{S}$ - $\text{SO}_4^{2-}$  and  $\delta^{18}\text{O}$ - $\text{SO}_4^{2-}$ ) should be better able to constrain the sources of dissolved sulphate (Calmels et al., 2007; Rock and Mayer, 2009; Turchyn et al., 2013). Sulphate in the river is generally derived from several sources with different isotopic compositions, such as atmospheric deposition, dissolution of evaporites, sulphide oxidation and anthropogenic inputs (Krouse and Mayer, 2000; Brenot et al., 2007; Rock and Mayer, 2009). Li et al. (2006) have reported that the  $\delta^{34}\text{S}$  values of rainwater have a range of  $+1.7\text{‰}$  to  $+5.6\text{‰}$  (average,  $+3.9\text{‰}$ ) in the Sichuan Basin without obvious seasonal variations. The oxygen isotope values of atmospheric sulphate generally have enriched  $^{18}\text{O}$  values due to the high contribution of air  $\text{O}_2$  to sulphate, which have shown that the  $\delta^{18}\text{O}$ - $\text{SO}_4^{2-}$  values ranged from  $+7\text{‰}$  to  $+17.2\text{‰}$  in previous studies (Krouse and Mayer, 2000; Brenot et al., 2007). In the studied area, there is a low content of  $\text{SO}_4^{2-}$  in the rain samples and river waters (Nos. 13 and 14) from the mountains mainly impacted by atmospheric input. The sulphate from the atmospheric input is estimated to be 6% of the sulphate flux in the Yalong River basin after correction by the  $\text{Cl}^-$  concentration of rain at Waliguan (Tang et al., 2000).

In the study area, shale and sparse sulphide minerals were observed during sampling, which could contribute to the sulphate content of the river. Waters (Nos. 5 and S7) from the small stream flowed through the area of exposed basalt belt and shale, have  $\delta^{34}\text{S}$ - $\text{SO}_4^{2-}$  values of  $-14\text{‰}$  and  $+1.6\text{‰}$ , respectively. The S isotopic compositions of sulphide minerals have a highly variable range from  $-13.3\text{‰}$  to  $+15.9\text{‰}$  in the mine located in the western Sichuan province (Yang et al., 2009). Thus, the  $\delta^{34}\text{S}_{\text{sulphide}}$  values



would have a wide range in this study. The sulphate originating from sulphide oxidation is expected to inherit the S isotopic composition of the precursor, and the  $^{18}\text{O}\text{-SO}_4^{2-}$  values are generally below 10‰ in the surface environment (Krouse and Mayer, 2000). Two main oxidation processes are involved in the sulphide oxidation, including air oxygen and  $\text{Fe}^{3+}$  (Taylor et al., 1984; van Everdingen and Krouse, 1985).

In the first pathway (Eq. (1)), the new sulphate would derive 7/8 of oxygen from air and one eighth from water. The second pathway (Eq. (2)) indicates that the oxygen of the new sulphate may only be derived from the water oxygen.



The  $\delta^{18}\text{O}$  of sulphate from sulphide oxidation can be assessed by oxygen source and the enrichment factors under different condition (van Everdingen and Krouse, 1985). The isotopic composition of air oxygen is approximately +23.5‰ (Kroopnick and Craig, 1972). The enrichment factors for  $\epsilon^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  and  $\epsilon^{18}\text{O}_{\text{SO}_4\text{-O}_2}$  could be assigned as 4.1‰ and -11.4‰, respectively (Taylor et al., 1984; van Everdingen and Krouse, 1985). In the present study, the  $\delta^{18}\text{O}\text{-H}_2\text{O}$  in water samples from the Yalong River has a range from -16‰ to -12‰. Therefore, the  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values would primarily have a range of -16‰ to 9‰. The sulphate from geological gypsum dissolution generally has  $\delta^{18}\text{O}$  values above +10‰ (Turchyn and Schrag, 2006). The water of the mainstream has  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values lower than 0‰, which indicates that reduced sulphur compound oxidation should be a major source of sulphate in these rivers. Most samples with  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values below 0‰ have  $\delta^{34}\text{S}\text{-SO}_4^{2-}$  values lower than +5‰. Therefore, in this study, the sulphur isotopes of the sulphate from oxidation can be assigned values from -14‰ to +5‰ (Fig. 4).

In the studied area, most hot springs have sulphate contents below 200  $\mu\text{mol/l}$  and low  $\text{SO}_4^{2-}/\text{Na}^+$  ratios with a median value of 0.03 based on water chemical analysis of hot springs sampled in the western Sichuan province (Zhang and Hu, 2000; Gao et al., 2004). The discharge of the total known hot spring waters in the entire basin is estimated to be  $1.3 \times 10^7 \text{ m}^3/\text{yr}^{-1}$  from geological survey reports of Sichuan province (Luo, 1994), suggesting that the known hot spring flux only contributed approximately 0.2‰ to the water source of the Yalong River. Thus, the sulphate from the hot springs of the Yalong River could be ignored. Meanwhile,

the contribution of chemical fertilisers was of minor importance for riverine sulphate due to low agricultural activities in the basin.

The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values increase downstream, which indicate that another sulphate source with high dual isotopic values contributed to the mainstream. The isotopic compositions of gypsum vary with the geological time ranging from +10‰ to +30‰ for  $\delta^{34}\text{S}$  and from +10‰ to +20‰ for  $\delta^{18}\text{O}$ , respectively (Claypool et al., 1980; Turchyn and Schrag, 2006). It was reported that the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values were +11‰ and +8‰ for sulphate mainly from evaporites in Jinsha Jiang, upstream from the Changjiang River (Liu et al., 2009). The slight positive correlation ( $R^2 = 0.36$ ) between  $\delta^{34}\text{S}\text{-SO}_4^{2-}$  and  $\text{SO}_4^{2-}$  concentration (Fig. 4) is found in river waters having relatively high  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values. This suggests that the isotopic compositions of sulphate in these rivers might be influenced by sulphate with heavy isotopes. The water in the Anning River has high  $\text{SO}_4^{2-}$  content with high  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values of +12‰ and +8.2‰ (No. 27), respectively, indicating evaporites as the major source of sulphate for the river.

As indicated by Fig. 4, the different sulphate sources can be quantified by the mixing diagram (Calmels et al., 2007). Thus, the contribution from different endmembers could be calculated after the atmospheric correction (Spence and Telmer, 2005):

$$[\text{SO}_4] = [\text{SO}_4]_{\text{atm}} + [\text{SO}_4]_{\text{sulphide}} + [\text{SO}_4]_{\text{evap}} \quad (3)$$

$$\delta^{34}\text{S}_{\text{river}}^* = \delta^{34}\text{S}_{\text{sulphide}} \times (a + b) + \delta^{34}\text{S}_{\text{evap}} \times (1 - a - b) \quad (4)$$

$$\delta^{18}\text{O}_{\text{river}}^* = \delta^{18}\text{O}_{\text{sulphide}} \times (a + b) + \delta^{18}\text{O}_{\text{evap}} \times (1 - a - b) \quad (5)$$

where  $(a + b)$  is the proportion of the total sulphate derived from oxidation of sulphide with different isotopic characteristics. In this study, the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  value from evaporites can be assigned as +16‰ and +12‰ according to above discussion. The calculated results suggest that the water in the upper reach of the Yalong River has a high proportion of sulphate originating from sulphide oxidation and there are 65–98% of sulphate from sulphide oxidation for the main channel of the Yalong River. Between 31% and 93% sulphate is derived from sulphide oxidation for the major tributaries. There is a high contribution of sulphate from sulphide oxidation in the Litang and Xianshui Rivers. The Anning River has a high proportion of sulphate from the gypsum inputs, which is close to 63%. The proportion of sulphate from the oxidation of sulphide (72%) in the Yalong River is lower than that in the Fraser River (81%, Spence and Telmer, 2005), and that of the Mackenzie River (82%, Calmels et al., 2007), but is higher than that in the Jialing River of the Changjiang Basin (16–56%, Li et al., 2011).

#### 4.2. Carbon dynamics constrained by $\delta^{13}\text{C}\text{-DIC}$ in the Yalong River

The DIC in the river mainly originate from  $\text{CO}_2$  recharge and carbonate dissolution, and are affected by respiration and decomposition of organic matter in waters, in situ photosynthesis and equilibration with the atmospheric  $\text{CO}_2$  (Yang et al., 1996; Galy and France-Lanord, 1999; Karim and Veizer, 2000; Das et al., 2005; Singh et al., 2005; Li et al., 2010). The first DIC source originates from the atmospheric  $\text{CO}_2$  dissolution via rain. Approximately 10  $\mu\text{mol/l}$   $\text{CO}_2$  dissolved in the water calculated by the equilibrium equations (Clark and Fritz, 1997). The low contents (0.14 mmol–0.33 mmol/l) of  $\text{HCO}_3^-$  were observed in the alpine lake and creek water, which should be 14–20 times higher than those of rainwater. Thus, atmospheric  $\text{CO}_2$  is not likely to be the major source of dissolved inorganic carbon in the river.

In fact, soil  $\text{CO}_2$  is the major weathering agent involved in carbonate and silicate weathering and fixed as DIC in most of the river waters (Das et al., 2005; Li et al., 2010). The soil  $\text{CO}_2$  would inherit

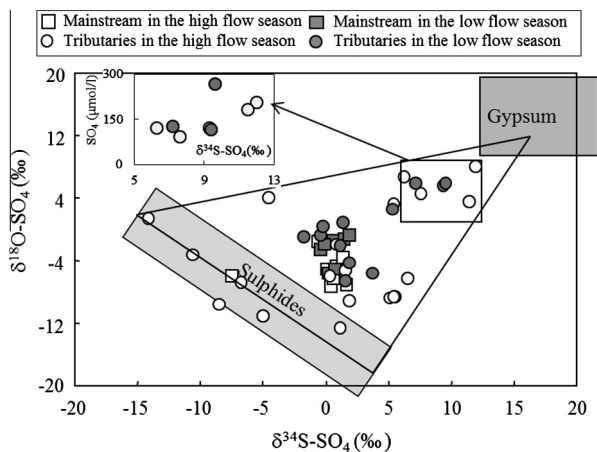


Fig. 4.  $\delta^{18}\text{O}\text{-SO}_4$  vs.  $\delta^{34}\text{S}\text{-SO}_4$  for waters in the Yalong River, China. The isotopic composition of the sources in the diagram (modified after references of Krouse and Mayer (2000), Calmels et al. (2007), and Liu et al. (2009)).

the carbon isotopic characteristics of organic matter (Cerling et al., 1991). Most C3 plants have  $\delta^{13}\text{C}$  values ranging from  $-24\text{‰}$  to  $-30\text{‰}$  (Vogel, 1993). In this study, the mean  $\delta^{13}\text{C}$ -POC of  $-24.4 \pm 1\text{‰}$  indicates that the organic matter is mainly derived from the C3 plants.  $\text{CO}_2$  diffusion would cause a slight enrichment ( $+4.4\text{‰}$ ) of the  $^{13}\text{C}$  in the soil  $\text{CO}_2$  relative to organic matter (Cerling et al., 1991). Sparse and thin soils distributed in the upper reach due to cold and dry conditions and in the middle reach due to the steep terrain. If the DIC only derived from soil  $\text{CO}_2$ , the  $\delta^{13}\text{C}$ -DIC values would be close to  $-20\text{‰}$ . In this study, the mean  $\delta^{13}\text{C}$  values of PIC mainly derived from carbonate are approximately  $-2 \pm 1\text{‰}$ . Thus, silicate weathering by soil  $\text{CO}_2$  should yield  $\delta^{13}\text{C}$ -DIC value close to  $-20\text{‰}$ , and carbonate dissolution should produce  $\delta^{13}\text{C}$ -DIC value of  $-11\text{‰}$ , because half of the  $\text{HCO}_3^-$  originates from the carbonate.  $\delta^{13}\text{C}$ -DIC value should be close to  $-2\text{‰}$  if the DIC is only derived from carbonate weathering by sulphuric acid (Spence and Telmer, 2005; Li et al., 2008).

Most water in this basin has  $\delta^{13}\text{C}$ -DIC values from  $-8\text{‰}$  to  $-5\text{‰}$  in the high flow season and from  $-7\text{‰}$  to  $-3\text{‰}$  in the low flow season, indicating the effect of many factors on the carbon isotopic composition of dissolved inorganic carbon. The role of strong acids such as sulphuric acid derived from sulphide oxidation in enhancing carbonate weathering has been recorded in many rivers (Spence and Telmer, 2005; Calmels et al., 2007; Li et al., 2008). Several rivers with relatively high  $\delta^{13}\text{C}$ -DIC values in the high flow seasons have high  $\text{SO}_4/\text{HCO}_3^-$  equivalent ratios above 0.5, such as Nos. 4 and 5, which suggested that the weathering of carbonate by sulphuric acid should contribute  $\text{HCO}_3^-$  to these rivers. Meanwhile, Fig. 5 shows the correlation between  $\delta^{13}\text{C}$ -DIC and  $\delta^{34}\text{S}$ - $\text{SO}_4$  in the Yalong River. Decreasing  $\delta^{34}\text{S}$ - $\text{SO}_4$  values with increasing  $\delta^{13}\text{C}$ -DIC values are observed, which supports that carbonate weathering by oxidation of sulphide contributes dissolved inorganic carbon to the waters significantly in the Yalong River.  $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$  ( $\delta^{18}\text{O}_{\text{SO}_4} - \delta^{18}\text{O}_{\text{H}_2\text{O}}$ ) can be a proxy of oxidation pathways of sulphide. In the anoxic environment, the oxidation of sulphide by  $\text{Fe}^{3+}$  (Eq. (2)) can produce low  $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$  values (Calmels et al., 2007). The negative correlations between  $\delta^{13}\text{C}$ -DIC and  $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$  were observed (Fig. 6). The water with low  $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$  and high  $\delta^{13}\text{C}$ -DIC values generally locate at high altitude areas of the Yalong River basin, which indicate the sulphuric acid as weathering agent plays a dominant role in carbonate weathering in these rivers. Furthermore, the recharge from soil  $\text{CO}_2$  derived from organic matter might be limited during cold and dry climate in the areas with high elevation, leading to high  $\delta^{13}\text{C}$ -DIC values observed in the waters.

In this study, the sampled hot spring has a  $\delta^{13}\text{C}$ -DIC value of  $0.9\text{‰}$ , which is within a range of  $-3.6\text{‰}$  to  $2.8\text{‰}$  for the hot springs

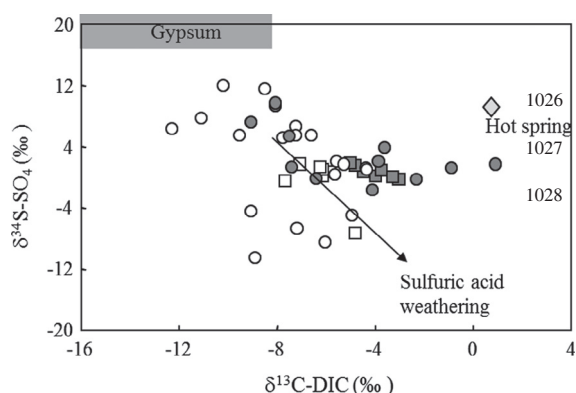


Fig. 5. Scatter diagram of  $\delta^{13}\text{C}$ -DIC vs.  $\delta^{34}\text{S}$ - $\text{SO}_4$  in the Yalong River. Symbols are the same as those in Fig. 4.

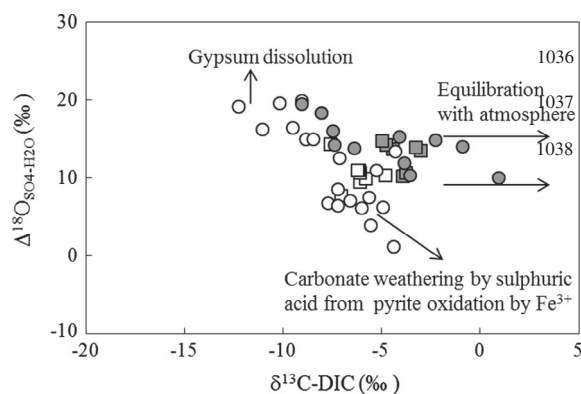


Fig. 6. Scatter diagram of  $\delta^{13}\text{C}$ -DIC vs.  $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$  in waters draining the Yalong River. Symbols are the same as those in Fig. 4.

at the Kangding of the Xianshui fault zone reported by Yang et al. (1999). The hot spring discharge into the river water may increase the  $\delta^{13}\text{C}$ -DIC values of the river water. In addition, the hot springs in the western Sichuan province generally have high  $\text{Na}^+$  and  $\text{Na}/\text{HCO}_3^-$  ratios. The river waters generally have lower  $\delta^{13}\text{C}$ -DIC values and  $\text{Na}/\text{HCO}_3^-$  ratios, which suggest that the hot spring should contribute minor DIC in the rivers regardless of  $^{13}\text{C}$  enriched in some water.

The physical and biological processes may shift  $\delta^{13}\text{C}$ -DIC values in rivers, such as degassing due to supersaturated condition, photosynthetic activity and  $\text{CO}_2$  equilibration with atmosphere (Yang et al., 1996). High  $p\text{CO}_2$  in the water has been shown to be controlled by soil  $\text{CO}_2$  recharge and could be partly consumed by rock weathering. High soil  $\text{CO}_2$  recharge might lead to the DIC enriched in light isotopes through the oxidation of organic matter. In general, there are 1–4 times supersaturated with respect to the atmosphere in the Yalong River. As indicated by Fig. 7, a negative trend ( $R^2 = 0.44$ ) is observed between the  $\delta^{13}\text{C}$ -DIC and  $p\text{CO}_2(\text{water})/p\text{CO}_2(\text{air})$  in the waters during the high flow season. The water with high  $p\text{CO}_2(\text{water})/p\text{CO}_2(\text{air})$  ratios and low  $\delta^{13}\text{C}$ -DIC values indicate that biological  $\text{CO}_2$  compose the major source of DIC in these waters. The degassing will only increase the  $\delta^{13}\text{C}$ -DIC values to about  $0.5\text{‰}$  (Zhang et al., 1995). The algae normally prefer to take up light isotopes, leading an enrichment of  $^{13}\text{C}$  in remaining DIC, especially in lake and reservoirs (Yang et al., 1996). The Ertan reservoir is located between No. 28 and No. 32 in the Yalong River. However, the water of No. 32 after the dam does not have higher  $\delta^{13}\text{C}$ -DIC values than that of the water of No. 28 before the dam, which suggest that photosynthetic activity may not be the reason for the shift in  $\delta^{13}\text{C}$ -DIC values in the sampling period. The cold climate of this area and the low nutrient

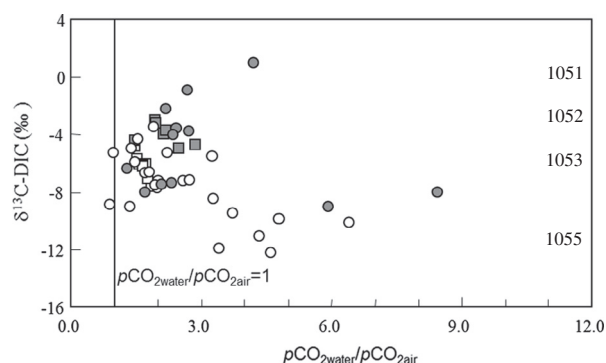


Fig. 7. Plots of  $\delta^{13}\text{C}$ -DIC vs.  $p\text{CO}_2(\text{water})/p\text{CO}_2(\text{air})$  ratios (atm) in the Yalong River. Symbols are the same as those in Fig. 4.

levels in the waters might not support intensive aquatic photosynthesis for increasing  $\delta^{13}\text{C}$ -DIC values.

The water from the mainstream has higher  $\delta^{13}\text{C}$ -DIC values by approximately 2‰ during the low-flow season in comparison to that during the high-flow season, which is in agreement with findings of other studies (Galy and France-lanord, 1999; Karim and Veizer, 2000; Li et al., 2010). The increasing  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations with decreasing  $\text{SO}_4^{2-}$  in the low-flow season indicate that the intensive carbonate weathering by sulphuric acid is not the major reason for the seasonal variations of  $\delta^{13}\text{C}$ -DIC values. The river water in complete equilibrium with the atmospheric  $\text{CO}_2$  should produce  $\delta^{13}\text{C}$ -DIC about 0‰ according the carbon isotopic fractionation during gas–water exchange (Zhang et al., 1995; Yang et al., 1996). As shown in Fig. 7, the high  $\delta^{13}\text{C}$ -DIC values and low  $p\text{CO}_2$  indicate that the equilibration between the atmospheric  $\text{CO}_2$  and the  $\text{HCO}_3^-$  influences the carbon isotopic composition of DIC in the waters. In this investigation, the  $\text{CO}_2$  equilibration with atmosphere could be the reason for DIC enriched in  $^{13}\text{C}$  due to the slow water flow and relatively long residence time of water in the low flow season with less rain, especially where the river flows through broad valleys and alpine plains.

#### 4.3. Chemical erosion and $\text{CO}_2$ consumption by weathering in the Yalong River

##### 4.3.1. Source of dissolved load and determination of endmembers

The dissolved load in rivers is mainly derived from atmospheric input, chemical weathering of carbonate, silicate and evaporite, and anthropogenic input (Gaillardet et al., 1999; Chetelat et al., 2008). The  $\text{Cl}^-$  normalised ratios of the rain water have been used to correct the dissolved load of rivers for the atmospheric input (Gaillardet et al., 1999). The  $\text{Cl}^-$  content of the two rain water samples collected in this study is about 1  $\mu\text{mol/l}$ . The two tributaries with elevation of above 3900 m have the lowest  $\text{Cl}^-$  contents. Several other tributaries (Nos. 5, 6, 10, and 17) directly enter the main channel of the Yalong River with the  $\text{Cl}^-$  contents of approximately 6  $\mu\text{mol/l}$ , which is equal to the mean value of  $\text{Cl}^-$  from 59 rain samples at Mt. Waliguan (36°17'N, 100°54'E) in the Tibetan Plateau (China Global Atmosphere Water Baseline Observatory, Tang et al., 2000). Therefore,  $[\text{Cl}]_{\text{atm}}$  can be assumed to be 6  $\mu\text{mol/l}$ . The solute contribution from the atmospheric inputs can be corrected based on ratios of ions vs.  $[\text{Cl}]$  in rain. The calculated results demonstrate that the contribution of  $\text{TZ}^+$  derived from precipitation to total  $\text{TZ}^+$  is below 3% in the mainstream of the Yalong River.

Carbonate weathering will contribute high  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  contents to the river waters from the quick dissolution of carbonate (Li et al., 2008, 2010; Han et al., 2010), which leads to the high  $\text{Ca}/\text{Na}$ ,  $\text{Mg}/\text{Na}$  and  $\text{HCO}_3^-/\text{Na}$  ratios in rivers. In this study,  $\text{Ca}$  and  $\text{Mg}$  were the major cations, which suggested that carbonate weathering contributed the major dissolved load for the rivers. The  $\text{Ca}/\text{Na}$  ratios have a range of 1.3–16 with a mean value of 5.6 indicating dominant  $\text{Ca}$  input from carbonate weathering. For evaporite endmembers, normalised  $\text{Na}$  ratios from the Changjiang River (Chetelat et al., 2008) were used.

In the investigated area, the  $\text{Na}$  content of the dissolved load is generally higher than the  $\text{Cl}$  concentration. The corrected  $\text{Na}$  concentration ( $\text{Na}^+ = \text{Na} - \text{Cl}$ ) might be thus assumed to be derived from silicate weathering. As  $\text{K}$  and  $\text{Si}$  are generally attributed to silicate weathering, the  $\text{Si}/(\text{Na}^+ + \text{K})$  ratio has been used as an index of silicate weathering intensity. Weathering of  $\text{Na}$ -feldspar to beidellite, to kaolinite and to gibbsite should produce a ratio of 1.7, 2.0 and 3.0, respectively (Huh et al., 1998). A positive correlation is observed ( $R^2 = 0.53$ ) between  $(\text{Na}^+ + \text{K})$  and  $\text{Si}$  in the river water samples indicating the influence of silicate weathering on the solutes budget (Fig. 8). The  $\text{Si}/(\text{Na}^+ + \text{K})$  ratio in most of the water

samples ranges from 0.5 to 3, which indicates that silicate weathering controls the inputs of  $\text{Na}$  and  $\text{K}$  to the rivers. The elemental ratios for the silicate end-member are taken to be the same as those listed by previous studies (Millot et al., 2003; Chetelat et al., 2008), which suggest that  $\text{Ca}/\text{Na}$ ,  $\text{Mg}/\text{Na}$  and  $\text{HCO}_3^-/\text{Na}$  are assigned to be approximately 0.35, 0.2, and 2, respectively. The elemental ratios of the different endmembers for calculation are listed in Table 1.

In this investigation, the sampled hot spring has a total dissolved solid (TDS) of 3000 mg/l. Meanwhile, the hot springs located at Daocheng and Kangding counties mainly belongs to the  $\text{Na}^+$ - $\text{HCO}_3^-$  and  $\text{Na}^+\cdot\text{Ca}^{2+}$ - $\text{HCO}_3^-$  types based on analysed contents of major ions (Zhang and Hu, 2000; Gao et al., 2004) and their chemical compositions differ from those measured in the rivers of the Yalong River basin (Fig. 3). Hot springs are widely distributed in the investigated area, especially near the Batang fault and the Xianshuihe fault, which should contribute load to the riverine solute budget. Along with a neutral pH, it displays very low  $\text{Ca}/\text{Na}$ ,  $\text{Mg}/\text{Na}$ ,  $\text{K}/\text{Na}$ ,  $\text{Cl}/\text{Na}$  and  $\text{SO}_4/\text{Na}$  ratios.  $\text{Na}$  accounts for more than 80% of the cationic charge and  $\text{HCO}_3^-$  is the dominant anion, indicating that high-temperature silicate alteration is the major source of solutes. The hot springs are mainly  $\text{Na}$ - $\text{HCO}_3^-$  and  $\text{Na}$ - $\text{Ca}$ - $\text{HCO}_3^-$  types, showing that  $\text{HCO}_3^-$  contents range from 5552  $\mu\text{mol/l}$  to 26,508  $\mu\text{mol/l}$ , with  $\text{Na}^+$  contents from 1696  $\mu\text{mol/l}$  to 20,861  $\mu\text{mol/l}$  and  $\text{Ca}^{2+}$  contents from 330  $\mu\text{mol/l}$  to 6595  $\mu\text{mol/l}$  in hot springs along Xianshuihe fault (Zhang and Hu, 2000). The hot springs in the Daocheng County along the Batang fault have  $\text{HCO}_3^-$  contents from 200  $\mu\text{mol/l}$  to 34,209  $\mu\text{mol/l}$ ; the  $\text{Na}$  contents from 774  $\mu\text{mol/l}$  to 27,391  $\mu\text{mol/l}$  and; the  $\text{Ca}$  contents from 100  $\mu\text{mol/l}$  to 7415  $\mu\text{mol/l}$  (Gao et al., 2004). The chemical data from those waters also show that the hot springs have low  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  contents. Among all the chemical data from the hot springs, the median values of the  $\text{HCO}_3^-/\text{Na}$ ,  $\text{Ca}/\text{Na}$ ,  $\text{Mg}/\text{Na}$  and  $\text{K}/\text{Na}$  ratios are listed in Table 1 and used for calculation.

$\text{NO}_3^-$  is derived from the anthropogenic input in the rivers. However, most waters have low  $\text{NO}_3^-$  contents in the Yalong River. The water from the Aning River (Nos. 24, 25, 26, 27, and 31) and another tributary (No. 30) at the lowland have slight higher contents of  $>10$   $\mu\text{mol/l}$   $\text{NO}_3^-$  than other rivers. The anthropogenic inputs can be ignored for the Yalong Rivers except the Anning River and the last outlet of the Yalong River (No. 33) due to the low population density in these areas. Chetelat et al. (2008) reported  $\text{Cl}/\text{Na}$  and  $\text{NO}_3^-/\text{Na}$  molar ratios of 5 and 4, respectively, for the agricultural end-member in the Changjiang River basin. These ratios are used to estimate anthropogenic inputs in this study.

##### 4.3.2. The quantitative contributions of the sources

The inverse model was used in this study to assess the relative contributions of the different end-members to the dissolved load

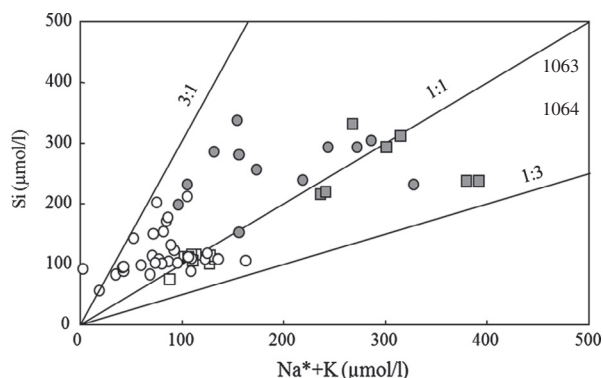


Fig. 8. Plots showing the relationship between  $[\text{Na}^+ + \text{K}]$  and  $\text{Si}$  for the waters collected from the Yalong River. Symbols are the same as those in Fig. 4.



**Table 1**

The ion ratios in different end-members for calculation in this study.

	Atmospheric	Evaporites	Carbonates	Silicates	Hot spring	Anthropogenic
Ca/Na	2 ± 1	0.17 ± 0.09	50 ± 20	0.35 ± 0.5	0.12 ± 3	0.00
Mg/Na	0.7 ± 0.3	0.02 ± 0.01	20 ± 12	0.2 ± 0.1	0.04 ± 1	0.00
K/Na	0.4 ± 1	0.00	0.00	0.17 ± 1	0.07 ± 0.1	0.2 ± 1
Cl/Na	1 ± 1	1.00	0.00	0.00	0.15 ± 0.5	2 ± 2
HCO <sub>3</sub> /Na	0.00	0.3 ± 0.3	120 ± 40	2 ± 1	1.2 ± 4	0.00
NO <sub>3</sub> /Na	1 ± 0.5	0.00	0.00	0.00	0.00	4 ± 1

See text for detail and refer to other studies (Millot et al., 2003; Chetelat et al., 2008).

and the calculated the drawdown of CO<sub>2</sub> by silicate weathering, which was based on a set of mass balance equations normalised to Na (Négrel et al., 1993; Gaillardet et al., 1999):

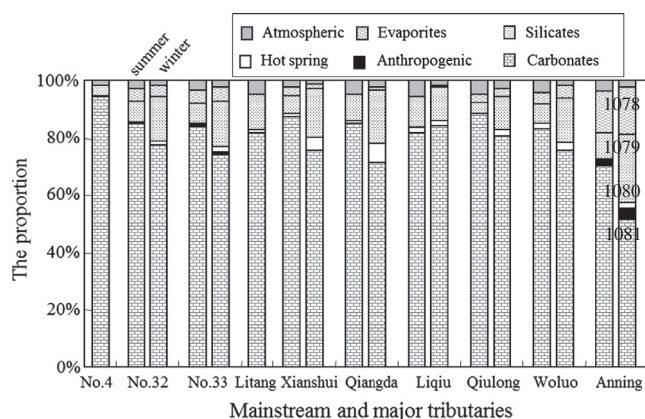
$$\left(\frac{X}{Na}\right)_{\text{river}} = \sum_i \left(\frac{X}{Na}\right)_i \alpha_i Na \quad (6)$$

$$\sum \alpha(Na)_i = 1 \quad (7)$$

where X stands for Ca, Mg, K, Cl, HCO<sub>3</sub> and NO<sub>3</sub>; *i* indicates the different source reservoirs (atmospheric input, carbonate, silicate, evaporites, hot spring and anthropogenic input) and;  $\alpha_{i,Na}$  means the mixing proportion of Na from the different reservoirs. The budget of sulphate was defined by dual isotopic method given in the previous discussion.

The contributions of the different sources to the dissolved cations (mg/l) calculated for the Yalong mainstream and major tributaries are shown in Fig. 9. The rivers in the Yalong River basin are dominated by carbonate weathering, which contributes between 51% and 94% of the cationic charge (μeq/l) in the rivers. For the whole basin, carbonate weathering contributes 83% of cations in the high flow season and 75% of cations in the low flow season to the Yalong River. The highest contribution from carbonate weathering is observed for the upper reach of the Yalong River (No. 4), which has high sulphate content derived from the oxidation of sulphide enhancing carbonate weathering.

The second major contribution was from silicate weathering, which accounted for 3% to 24% of cations to rivers. The lowest contribution is observed for the upper reach of the mainstream (No. 4). The Anning River has high silicate weathering contribution for the total dissolved cations, which showed that approximately 24% cations derived from silicate weathering for the river water in winter. At the outlets of the Yalong River, the contributions of silicate weathering are 8% in the high flow season and 16% in the low flow season, respectively. The major tributaries have high silicate weathering contribution relative to the upper reach of the Yalong

**Fig. 9.** The contributions of different sources to the total dissolved cations (mg/l) for the Yalong mainstream (Nos. 4, 32, and 33) and major tributaries.

River. The rivers in the low flow season generally have high contribution of cations from silicate weathering compared with those in the high flow season, which is similar to observations from previous studies (Tipper et al., 2006; Moon et al., 2007). The long water–rock interaction time in winter can cause a larger higher proportion of cations from silicate weathering (Tipper et al., 2006), which should be responsible for the seasonal variation in the contribution from silicate weathering due to less rainfall in the dry season.

Minor contribution to the cations comes from the atmospheric inputs, which in general has a range of 2% to 6%. For the outlets of the Yalong River, the contributions are between 3% in the high flow season and 2% in the low flow season. The contribution of the hot springs in the Yalong River was ignored in the previous studies (Chetelat et al., 2008; Wu et al., 2008), which accounted for 0.1–6.6% of cations to rivers. The seasonal variation of the contribution from hot springs is similar to that of silicate weathering. The contributions from hot spring are between 0.6% in the high flow season and 1.6% in the low flow season for the outlets of the Yalong River, respectively.

#### 4.3.3. CO<sub>2</sub> consumption and chemical weathering rates

The sulphuric acid derived from the oxidation of sulphide might take part in both the carbonate and silicate weathering. It is assumed that silicate and carbonate weathering by sulphuric acid occur in the same ratio as those by carbonic acid (Galy and France-Lanord, 1999). Thus, the mass balance equations can be written as (Spence and Telmer, 2005):

$$[SO_4]_{\text{sulphide}} = [SO_4]_{\text{SCW}} + [SO_4]_{\text{SSW}} \quad (8)$$

$$A \approx [TZ^+]_{\text{sil}}/[TZ^+]_{\text{carb}} = [SO_4]_{\text{SSW}}/[SO_4]_{\text{SCW}} \quad (9)$$

$$2[SO_4]_{\text{SCW}} = [HCO_3]_{\text{CSW}} \quad (10)$$

$[SO_4]_{\text{SCW}}$  and  $[SO_4]_{\text{SSW}}$  represent  $[SO_4]$  consumed by carbonate and silicate weathering, respectively.  $[HCO_3]_{\text{CSW}}$  represents HCO<sub>3</sub><sup>-</sup> from carbonate weathering by sulphuric acid. *A* is the ratio of sulphuric acid consumed by silicate weathering vs. sulphuric acid consumed by carbonate weathering. The calculated proportion of  $[HCO_3]_{\text{CSW}}$  in the Yalong River amounts to approximately 15% of DIC in the high flow season and 7% of the DIC in the low flow season, respectively. The CO<sub>2</sub> consumption by silicate weathering (CO<sub>2sil</sub>) and carbonate weathering (CO<sub>2carb</sub>) can be calculated based on the charge balance after different weathering agents were assessed:

$$CO_{2\text{sil}} = [TZ^+]_{\text{sil}} - 2 \times [SO_4]_{\text{SSW}} \quad (11)$$

$$CO_{2\text{carb}} = (2 \times [Ca + Mg]_{\text{carb}} - [HCO_3]_{\text{CSW}})/2 \quad (12)$$

The discharge in the high and low flow seasons are assigned as about 75% and 25% of the annual total discharge in the Yalong River, respectively. As listed in Table 2, the results of chemical weathering rates and CO<sub>2</sub> consumption for the mainstream and the major tributaries are calculated by the equations above and



**Table 2**  
Chemical weathering rates and CO<sub>2</sub> consumption as well as DIC contribution from hot spring for the Yalong Rivers.

Sample	River	Water discharge (m <sup>3</sup> /s)	Surface area (km <sup>2</sup> )	Rock weathering (ton/km <sup>2</sup> /yr)				CO <sub>2</sub> cons. – silicates		CO <sub>2</sub> cons. – carbonates		DIC from hot spring (10 <sup>9</sup> mol/year)
				Silicate	Carbonates	Evaporites + sulphide (S)	Total rock	10 <sup>9</sup> mol/year	10 <sup>5</sup> mol/km <sup>2</sup> /year	10 <sup>9</sup> mol/year	10 <sup>5</sup> mol/km <sup>2</sup> /year	
4	Yalong River, Ganzhi	276	32,925	1.8	47.3	5.4	54.5	0.54	0.16	7.56	2.30	0.12
32	Yalong River, Xiaodeshi	1670	117,040	5.9	42.2	4.7	52.8	10.03	0.86	32.83	2.81	0.84
33	Yalong River, Panzhihua	1914	128,444	6.5	42.0	5.6	54.1	11.83	0.92	36.09	2.81	1.05
12	Litang River	152	10,676	4.6	26.7	2.3	33.6	0.58	0.54	1.86	1.74	0.03
15	Xuanshui River	194	19,400	4.5	38.8	3.7	46.9	1.54	0.79	5.28	2.72	0.32
17	Qingda River	30	1870	7.2	34.0	2.0	43.3	0.19	1.04	0.41	2.19	0.03
19	Liqu River	148	5820	10.6	54.4	3.5	68.5	0.80	1.38	1.70	2.92	0.15
21	Jiulong River	107	3560	10.2	65.2	5.8	81.3	0.31	0.86	1.70	4.76	0.03
29	Woluo River	135	8440	6.6	38.9	5.1	50.6	0.72	0.85	2.06	2.44	0.13
31	Anning River	233	11,151	11.8	37.2	12.4	61.5	1.80	1.61	2.97	2.67	0.21

discharge. The HCO<sub>3</sub><sup>-</sup> from silicate weathering is approximately 50–138 μmol/l in the high flow season and 216–519 μmol/l in the low flow season, respectively, which suggests that CO<sub>2</sub> consumption by silicate weathering is approximately 11.8 × 10<sup>9</sup> mol/yr and 0.9 × 10<sup>5</sup> mol/km<sup>2</sup>/yr for the whole basin. The CO<sub>2</sub> flux consumed by silicate weathering in this study is lower than the calculated result at Yalong River by Wu et al. (2008). The major reason is that HCO<sub>3</sub><sup>-</sup> from hot spring and the carbonate weathering by sulphuric acid are considered in this study. Another possible reason might be various ion concentrations in water at different sampling periods. This result is close to other rivers originating in the eastern Tibetan plateau, such as the upper stream of the Yellow River with 0.9–1.2 × 10<sup>5</sup> mol/km<sup>2</sup>/yr (Wu et al., 2005), the Hong river with a value of 1.7 × 10<sup>5</sup> mol/km<sup>2</sup>/yr in summer and 0.6 × 10<sup>5</sup> mol/km<sup>2</sup>/yr in winter (Moon et al., 2007), the Chang Jiang (1.05 × 10<sup>5</sup> mol/km<sup>2</sup>/yr), Lancang (1.03 × 10<sup>5</sup> mol/km<sup>2</sup>/yr), Nu Jiang (1.21 × 10<sup>5</sup> mol/km<sup>2</sup>/yr) after the oxidation of sulphide ignored (Noh et al., 2009) and Min Jiang with a value of 0.3–2.5 × 10<sup>5</sup> mol/km<sup>2</sup>/yr (Yoon et al., 2008). For the tributaries, the CO<sub>2</sub> consumption rate by silicate weathering varies from 0.5 × 10<sup>5</sup> mol/km<sup>2</sup>/yr for the upper reach of Litang River to 1.6 × 10<sup>5</sup> mol/km<sup>2</sup>/yr for the Anning River. The result of the CO<sub>2</sub> consumption rate via silicate weathering in rivers in the eastern Tibetan Plateau is generally lower than that in rivers at the front Himalaya, such as Brahmaputra with a range of 0.2–15.2 × 10<sup>5</sup> mol/km<sup>2</sup>/yr (Hren et al., 2007), rivers draining the Tibet and eastern syntaxis in the Himalayas (0.7–19 × 10<sup>5</sup> mol/km<sup>2</sup>/yr) (Singh et al., 2005), Ganges–Brahmaputra basin approximately 1.6 × 10<sup>5</sup> mol/km<sup>2</sup>/yr (Galy and France-Lanord, 1999), Ganga approximately 2 × 10<sup>5</sup> mol/km<sup>2</sup>/yr and Yanuna river system of 4–7 × 10<sup>5</sup> mol/km<sup>2</sup>/yr (Dalai et al., 2002). The CO<sub>2</sub> consumption by carbonate weathering is 36.1 × 10<sup>9</sup> mol/yr and 2.8 × 10<sup>5</sup> mol/km<sup>2</sup>/yr. As for the tributaries, the CO<sub>2</sub> consumption due to carbonate weathering is 1.6–5.5 times that due to silicate weathering. The result of the consumption of CO<sub>2</sub> by carbonates is lower than that for Changjiang basin of 4 × 10<sup>5</sup> mol/km<sup>2</sup>/yr, which is 4 times greater than that by silicate weathering (Chetelat et al., 2008).

The chemical erosion rate within the Yalong River basin could be estimated from the contribution of ions from the different reservoirs. The rate of silicate weathering (TDS<sub>sil</sub>) is calculated using the cations from silicate weathering and dissolved Si, assuming that all in the river waters originated from silicate weathering. The rate of carbonate weathering (TDS<sub>carb</sub>) is calculated based on the Ca, Mg and HCO<sub>3</sub><sup>-</sup> only derived from carbonate. Carbonate and silicate weathering account for approximately 81% and 10% of the total cationic charge in the Yalong River, respectively. There are approximately 0.84 × 10<sup>6</sup> t/yr of dissolved materials originated from silicate weathering and approximately 5.4 × 10<sup>6</sup> t/yr of that from carbonate weathering transported from the outlets of the Yalong River. The weathering rates vary from 26.7 t/km<sup>2</sup>/yr to

65.2 t/km<sup>2</sup>/yr for carbonate in the Yalong River. The sum of the chemical weathering of silicate and carbonate is 48.5 t/km<sup>2</sup>/yr, which is higher than the global average value of 24 t/km<sup>2</sup>/yr (Gaillardet et al., 1999). For the tributaries, the total chemical weathering rate varies from 33.6 t/km<sup>2</sup>/yr of the Litang River to 81.3 t/km<sup>2</sup>/yr of the Jiulong River. The total chemical weathering of all the rocks including evaporites and pyrite(S) is 54.1 t/km<sup>2</sup>/yr for the Yalong River. The silicate weathering flux is from 1.8 t/km<sup>2</sup>/yr for the upper reach of the Yalong River to 11.8 t/km<sup>2</sup>/yr for the Anning River in the mainstream and major tributaries, with a 6.5 t/km<sup>2</sup>/yr for whole basin. The low silicate weathering rate in the upper reach of the Yalong River might be due to the cold and dry climate as well as the strath terrace. High precipitation and steep slopes in the middle and lower reaches of the Yalong River should be responsible for the high chemical weathering rates in the tributaries of middle and lower reaches.

#### 4.4. Implication for the regional carbon budget

There is 8.5 × 10<sup>9</sup> mol/yr of SO<sub>4</sub><sup>2-</sup> derived from pyrite oxidation in the Yalong River basin with 0.1% of global land area, amounting to 1.7% of global pyrite-derived sulphate flux into the ocean (Bernier and Bernier, 1996). The precipitation of carbonate in the ocean would lead to transient release of CO<sub>2</sub> to the atmosphere system because the residence time of SO<sub>4</sub> in the ocean is much longer than that of bicarbonate (10<sup>5</sup> yr) after HCO<sub>3</sub><sup>-</sup> from carbonate weathering by sulphuric acid transported into the ocean (Calmels et al., 2007). Thus, the same amount of CO<sub>2</sub> will be transiently released to the atmosphere, which accounts for 72% of CO<sub>2</sub> consumed by silicate weathering in this basin. From the perspective of the long term carbon cycle, the net CO<sub>2</sub> flux consumed by chemical weathering become very small due to the counterbalance by the transient CO<sub>2</sub> release. Other studies also revealed that sulphate in Himalayan rivers was mainly derived from oxidation of pyrite (Galy and France-Lanord, 1999; Karim and Veizer, 2000; Turchyn et al., 2013), which suggest that sulphide weathering in the Himalayan zone should influence the long-term carbon cycle due to oxidation of ubiquitous sulphide. Meanwhile, the result indicates that the net CO<sub>2</sub> consumed by silicate weathering might be overestimated in previous studies ignoring carbonate weathering by sulphide oxidation.

It is reported that the CO<sub>2</sub> from metamorphic fluid plays an important role for regional and global carbon budget at orogenic zones, especially in the Himalayas (Gaillardet and Galy, 2008). In the investigated area, the direct flux of CO<sub>2</sub> from the hot spring to the river is found to be 1 × 10<sup>9</sup> mol/yr, which is approximately 1/6 of the long term CO<sub>2</sub> sequestration by silicate weathering in the Yalong River. However, CO<sub>2</sub> degassing might far outweigh the direct flux of CO<sub>2</sub> to the river in the basin and lead to the remaining DIC enriched in <sup>13</sup>C (Becker et al., 2008; Evans et al., 2008). Becker

et al. (2008) suggested that  $>97 \pm 1\%$  CO<sub>2</sub> degassing from empirical and thermodynamic modelling in the Marsyandi Valley, Nepal. In this study, only one hot spring was measured for  $\delta^{13}\text{C-DIC}$  with a value of  $+0.9\text{‰}$ , which is far lower than the  $\delta^{13}\text{C-DIC}$  values of most hot springs in the Narayani basin up to  $+13\text{‰}$  (Evans et al., 2008). Yang et al. (1999) have reported that the hot springs have  $\delta^{13}\text{C-DIC}$  values ranging from  $-3.6\text{‰}$  to  $+2.8\text{‰}$  with a mean value of  $-0.56\text{‰}$  in the Kangding county located at Xianshui fault. Therefore, the proportion of CO<sub>2</sub> flux from degassing might not be large according to carbon isotopic proof in this studied area. It was estimated that there was approximately 40% of CO<sub>2</sub> degassing to atmosphere after calculation based on the water chemistry and carbon isotopes in the Kangding county (Yang et al., 1999). Thus, the metamorphic HCO<sub>3</sub><sup>-</sup> flux and CO<sub>2</sub> degassing may offset part of CO<sub>2</sub> sequestration by chemical weathering in different timescales, which should be taken into account for the carbon budget in the riverine system.

In the short term, organic carbon in aquatic systems could trap a large of anthropogenic carbon (Cole et al., 2007). The POC flux from the terrestrial ecosystem to inland waters could be  $1.7 \times 10^{10}$  mol/yr in the Yalong River according to the carbon content of No. 28 and annual average SPM ( $2.55 \times 10^7$  t/yr) flux in the Yalong River (Zhu, 2007), which amounts to 14% of the DIC flux. Approximately 90% of the SPM was trapped by the reservoirs (Feng et al., 2008), which indicated approximately  $1.5 \times 10^{10}$  mol/yr of POC would be buried in the sediments for days to hundred years or longer in the reservoir. The carbon dynamic and storage in the inland waters might be taken into account for the global and regional carbon cycle regardless that man-made reservoirs might be short lived (Cole et al., 2007). The flux of OC storage in the sediment might amount to approximately 25% of CO<sub>2</sub> consumption via silicate weathering in the Yalong River if it is assumed approximately 20% of OC buried for a relative long term (>100 years).

There are multiple factors controlling riverine carbon budget and thus the global carbon cycle (Gaillardet et al., 1999; West et al., 2005; Goudie and Viles, 2012). As discussion above, the rock weathering by strong acid from sulphide oxidation could influence the long term carbon cycle and the short term carbon budget is impacted by the metamorphic CO<sub>2</sub> release and organic carbon burial. Therefore, more studies including monitoring network in rivers are needed to investigate the accurate carbon budget and complete the regional and global carbon cycle.

## 5. Conclusions

The water sampling from the Yalong River at the eastern Tibetan Plateau was carried out for two seasons. The measured  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O-SO}_4$  and  $\delta^{13}\text{C-DIC}$ , together with water chemistry are used to estimate solute sources and chemical processes. The total dissolved solids (TDS) vary from 17 to 346 mg/l. The dominant cation (Ca<sup>2+</sup>) and anion (HCO<sub>3</sub><sup>-</sup>) are mainly derived from carbonate weathering. The chemical budget and dual isotopic compositions of sulphate indicate that approximately 72% of the sulphate originated from sulphide oxidation, which leads to  $\sim 13\%$  of the dissolved inorganic carbon from carbonate weathering by sulphuric acid in the Yalong River. The rivers with low  $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$  and high  $\delta^{13}\text{C-DIC}$  value are located at the area with high elevation in the Yalong River basin, which indicates that carbon dynamics is influenced by the dominant role of sulphuric acid in carbonate weathering and limited microbial oxidation of organic matter in the cold and dry zone. The chemical and carbon isotopic analysis suggest that the  $\delta^{13}\text{C-DIC}$  values in studied rivers are mainly affected by the carbonate weathering and equilibration with atmospheric CO<sub>2</sub>, especially in the low flow season. Carbonate and silicate weathering account for approximately 81% and 10%, respectively, of the total cationic charge in the Yalong River. The weathering rates vary from 1.8 t/km<sup>2</sup>/yr to 11.8 t/km<sup>2</sup>/yr for

silicate and 26.7 t/km<sup>2</sup>/yr to 65.2 t/km<sup>2</sup>/yr for carbonate, respectively. A low silicate weathering rate calculated for the upper Yalong River is probably related to the cold and dry climate. The CO<sub>2</sub> consumption rate via silicate weathering for the whole basin is  $\sim 0.9 \times 10^5$  mol/km<sup>2</sup>/yr after considering the DIC from hot spring and the rock weathering via sulphuric acid, which is close to that calculated for the other rivers draining the eastern Tibetan Plateau but is lower than that for the rivers of eastern syntaxis and southern slopes of Himalaya with high runoff. Clearly, there is non-negligible influence from metamorphic CO<sub>2</sub> and carbonate weathering by sulphide oxidation on the riverine carbon budget at Himalayan zones.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jseas.2014.03.011>.

## References

- Atekwana, E.A., Krishnamurthy, R.V., 1998. Seasonal variations of dissolved inorganic carbon and  $\delta^{13}\text{C}$  of surface waters: application of a modified gas evolution technique. *J. Hydrol.* 205, 265–278.
- Becker, J.A., Bickle, M.J., Galy, A., Holland, T.J.B., 2008. Himalayan metamorphic CO<sub>2</sub> fluxes: quantitative constraints from hydrothermal springs. *Earth Planet. Sci. Lett.* 265, 616–629.
- Berner, K.E., Berner, R.A., 1996. *Global Environment: Water, Air and Geochemical Cycles*. Prentice Hall, Upper Saddle River, New Jersey.
- Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate–silicate geochemical cycle and its effect on atmospheric carbon-dioxide over the past 100 million years. *Am. J. Sci.* 283, 641–683.
- Brenot, A., Carignan, J., France-Lanord, C., Benoit, M., 2007. Geological and land use control on  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of river dissolved sulfate: the Moselle River Basin, France. *Chem. Geol.* 244, 25–41.
- Bureau of Geology, Mineral Resources of Sichuan Province, 1991. *Regional Geology of Sichuan Province*. Geological Publishing House, Beijing (in Chinese).
- Calmels, D., Gaillardet, J., Brenot, A., France-Lanord, C., 2007. Sustained sulfide oxidation by physical erosion processes in the Mackenzie River Basin: climatic perspectives. *Geology* 35, 1003–1006.
- Cen, S., Qin, N., Li, Y., 2012. Climatic characteristics of runoff variation in flood season in Jinsha River Basin. *Resour. Sci.* 34, 1538–1545 (in Chinese with English abstract).
- Cerling, T.E., Solomon, D.K., Quade, J., Bowman, J.R., 1991. On the isotopic composition of carbon in soil carbon dioxide. *Geochim. Cosmochim. Acta* 55, 3403–3405.
- Chetelat, B., Liu, C.-Q., Zhao, Z.Q., Wang, Q.L., Li, S.L., Li, J., Wang, B.L., 2008. Geochemistry of the dissolved load of the Changjiang Basin rivers: anthropogenic impacts and chemical weathering. *Geochim. Cosmochim. Acta* 72, 4254–4277.
- Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves for sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.* 28, 199–260.
- Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tanvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., Melack, J., 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* 10, 171–184.
- Dalai, T.K., Krishnaswami, S., Sarin, M.M., 2002. Major ion chemistry in the headwaters of the Yamuna river system: chemical weathering its temperature dependence and CO<sub>2</sub> consumption in the Himalaya. *Geochim. Cosmochim. Acta* 66, 3397–3416.

- Das, A., Krishnaswami, S., Bhattacharya, S.K., 2005. Carbon isotope ratio of dissolved inorganic carbon DIC in rivers draining the Deccan Traps, India: sources of DIC and their magnitudes. *Earth Planet. Sci. Lett.* 236, 419–429.
- Evans, M.J., Derry, L.A., France-Lanord, C., 2008. Degassing of metamorphic carbon dioxide from the Nepal Himalaya. *Geochem. Geophys. Geosyst.* 9, 1–16.
- Feng, X., Yang, Q., Zhang, O., Wang, X., 2008. Sediment trap of Ertan Reservoir and its effect on sediment budget of Jinsha River. *J. Sichuan Univ.* 40, 37–42 (in Chinese with English abstract).
- France-Lanord, C., Derry, L.A., 1997. Organic carbon burial forcing of the carbon cycle from Himalayan erosion. *Nature* 390, 65–67.
- Gaillardet, J., Galy, A., 2008. Himalaya, carbon sink or source? *Science* 320, 1727–1728.
- Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO<sub>2</sub> consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.
- Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges–Brahmaputra basin and the riverine alkalinity budget. *Chem. Geol.* 159, 31–60.
- Gao, Z., Yin, G., Fan, X., Wu, H., Wang, Q., Hou, M., 2004. Distribution characteristics of geothermal resources and isotopic geochemistry of hot water in the Daocheng County, Sichuan Province. *Bull. Mineral. Petrol. Geochem.* 23, 134–139 (in Chinese with English abstract).
- Goudie, A.S., Viles, H.A., 2012. Weathering and global carbon cycle: geomorphological perspectives. *Earth-Sci. Rev.* 113, 59–71.
- Han, G., Tang, Y., Xu, Z., 2010. Fluvial geochemistry of rivers draining karst terrain in Southwest China. *J. Asian Earth Sci.* 38, 65–75.
- Hren, M.T., Chamberlain, C.P., Hillel, G.E., Blisniuk, P.M., Bookhagen, B., 2007. Major ion chemistry of the Yarlung Tsangpo–Brahmaputra river: chemical weathering, erosion, and CO<sub>2</sub> consumption in the southern Tibetan plateau and eastern Syntaxis of the Himalaya. *Geochim. Cosmochim. Acta* 71, 2907–2935.
- Huh, Y., Tsoi, M.Y., Zaitsev, A., Edmond, J.M., 1998. The fluvial geochemistry of the rivers of Eastern Siberia: I. Tributaries of the Lena River draining the sedimentary platform of the Siberian Craton. *Geochim. Cosmochim. Acta* 62, 1657–1676.
- Jacobson, A.D., Blum, J.D., Walter, L.M., 2002. Reconciling the elemental and Sr isotope composition of Himalayan weathering fluxes: insights from the carbonate geochemistry of stream waters. *Geochim. Cosmochim. Acta* 66, 3417–3429.
- Karim, A., Veizer, J., 2000. Weathering processes in the Indus River Basin: implications from riverine carbon, sulfur, oxygen, and strontium isotopes. *Chem. Geol.* 170, 153–177.
- Kroopnick, P.M., Craig, H., 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science* 175, 54–55.
- Krouse, H.R., Mayer, B., 2000. Sulphur and oxygen isotopes in sulfate. In: Cook, P.G., Herczeg, A.L. (Eds.), *Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Publishers, USA, pp. 195–231.
- Li, X.D., Masuda, H., Kusakabe, M., Yanagisawa, F., Zeng, H.A., 2006. Degradation of groundwater quality due to anthropogenic sulfur and nitrogen contamination in the Sichuan Basin, China. *Geochem. J.* 40, 309–332.
- Li, S.-L., Calmels, D., Han, G., Gaillardet, J., Liu, C.-Q., 2008. Sulfuric acid as an agent of carbonate weathering constrained by  $\delta^{13}\text{C}_{\text{DIC}}$ : examples from Southwest China. *Earth Planet. Sci. Lett.* 270, 189–199.
- Li, S.-L., Liu, C.-Q., Li, J., Lang, Y.-C., Ding, H., Li, L., 2010. Geochemistry of dissolved inorganic carbon and carbonate weathering in a small typical karstic catchment of Southwest China: isotopic and chemical constraints. *Chem. Geol.* 277, 301–309.
- Li, X.-D., Liu, C.-Q., Liu, X.-L., Bao, L.-R., 2011. Identification of dissolved sulfate sources and the role of sulfuric acid in carbonate weathering using dual-isotopic data from the Jialing River, Southwest China. *J. Asian Earth Sci.* 42, 370–380.
- Liu, C.-Q., Lang, Y.-C., Strauss, H., Chetelat, B., Li, S.-L., Wang, B.-L., Li, J., 2009. Variation in content and isotopic composition of sulfate in Changjiang Yangtze River water. *Geochim. Cosmochim. Acta* 73 (Goldschmidt Conference Abstracts, Switzerland, A775).
- Ludwig, W., Amiotte-Suchet, P., Munhoven, G., Probst, J.-L., 1998. Atmospheric CO<sub>2</sub> consumption by continental erosion: present-day controls and implications for the last glacial maximum. *Global Planet. Change* 16–17, 107–120.
- Luo, L., 1994. The first study on origin and distribution of hot springs, West Sichuan Province. *J. Chongqing Teach. Coll.* 11, 39–47 (in Chinese).
- Millot, R., Gaillardet, J., Dupré, B., Allègre, C.J., 2003. Northern latitude chemical weathering rates: clues from the Mackenzie River Basin, Canada. *Geochim. Cosmochim. Acta* 67, 1305–1329.
- Moon, S., Huh, Y., Qin, J., van Pho, N., 2007. Chemical weathering in the Hong Red River basin: rates of silicate weathering and their controlling factors. *Geochim. Cosmochim. Acta* 71, 1411–1430.
- Négrel, P., Allegre, C.J., Dupré, B., Lewin, E., 1993. Erosion sources determined by inversion of major and trace element ratios in river waters: the Congo Basin case. *Earth Planet. Sci. Lett.* 120, 59–76.
- Noh, H., Huh, Y., Qin, J., Ellis, A., 2009. Chemical weathering in the Three Rivers region of Eastern Tibet. *Geochim. Cosmochim. Acta* 73, 1857–1877.
- Qin, J., Huh, Y., Edmond, J.M., Du, G., Ran, J., 2006. Chemical and physical weathering in the Min Jiang, a headwater tributary of the Yangtze River. *Chem. Geol.* 227, 53–69.
- Raymo, M.E., Ruddiman, W.F., 1992. Tectonic forcing of late Cenozoic climate. *Nature* 359, 117–122.
- Rock, L., Mayer, B., 2009. Identifying the influence of geology, land use, and anthropogenic activities on riverine sulfate on a watershed scale by combining hydrometric, chemical and isotopic approaches. *Chem. Geol.* 262, 121–130.
- Singh, S.K., Sarin, M.M., France-Lanord, C., 2005. Chemical erosion in the eastern Himalaya: major ion composition of the Brahmaputra and  $\delta^{13}\text{C}$  of dissolved inorganic carbon. *Geochim. Cosmochim. Acta* 69, 3573–3588.
- Spence, J., Telmer, K., 2005. The role of sulfur in chemical weathering and atmospheric CO<sub>2</sub> fluxes: evidence from major ions,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$  in rivers of the Canadian Cordillera. *Geochim. Cosmochim. Acta* 69, 5441–5458.
- Tang, J., Xue, H., Yu, X., Cheng, H., Xu, X., Zhang, X., Ji, J., 2000. The preliminary study on chemical characteristics of precipitation at Mt. Waliguan. *Acta Sci. Circums.* 20, 420–425 (in Chinese with English abstract).
- Taylor, B.E., Wheeler, M.C., Nordstrom, D.K., 1984. Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. *Geochim. Cosmochim. Acta* 48, 2669–2678.
- Tipper, E.T., Bickle, M., Galy, A., West, A.J., Pomiès, C., Chapman, H.J., 2006. The short term climatic sensitivity of carbonate and silicate weathering fluxes: insight from seasonal variations in river chemistry. *Geochim. Cosmochim. Acta* 70, 2737–2754.
- Turchyn, A.V., Schrag, D.P., 2006. Cenozoic evolution of the sulfur cycle: insight from oxygen isotopes in marine sulfate. *Earth Planet. Sci. Lett.* 241, 763–779.
- Turchyn, A.V., Tipper, E.T., Galy, A., Lo, J.-K., Bickle, M.J., 2013. Isotope evidence for secondary sulfide precipitation along the Marsyandi River, Nepal, Himalayas. *Earth Planet. Sci. Lett.* 374, 36–46.
- Van Everdingen, R.O., Krouse, H.R., 1985. Isotope composition of sulphates generated by bacterial and abiological oxidation. *Nature* 315, 395–396.
- Vogel, J.C., 1993. Variability of carbon isotope fractionation during photosynthesis. In: Ehleringer, J.R., Hall, A.E., Farquhar, G.D. (Eds.), *Stable Isotope and Plant Carbon – Water Relations*. Academic Press, San Diego, pp. 29–46.
- West, A.J., Galy, A., Bickle, M., 2005. Tectonic and climatic controls on silicate weathering. *Earth Planet. Sci. Lett.* 235, 211–228.
- Wu, L., Huh, Y., Qin, J., Du, G., van Der Lee, S., 2005. Chemical weathering in the Upper Huang He (Yellow River) draining the eastern Qinghai-Tibet Plateau. *Geochim. Cosmochim. Acta* 69, 5279–5294.
- Wu, W., Xu, S., Yang, J., Yin, H., 2008. Silicate weathering and CO<sub>2</sub> consumption deduced from the seven Chinese rivers originating in the Qinghai-Tibet Plateau. *Chem. Geol.* 249, 307–320.
- Yang, C., Telmer, K., Veizer, J., 1996. Chemical dynamics of the “St. Lawrence” riverine system:  $\delta\text{D}_{\text{H}_2\text{O}}$ ,  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{34}\text{S}_{\text{sulfate}}$ , and dissolved  $^{87}\text{Sr}/^{86}\text{Sr}$ . *Geochim. Cosmochim. Acta* 60, 851–866.
- Yang, L., Wei, J., Sun, J., 1999. A study of the Deep-Source CO<sub>2</sub> release of the hot springs system in Kangding, Sichuan Province. *Acta Geol. Sinica* 73, 279–285 (in Chinese with English abstract).
- Yang, Z., Qiu, R., Qin, S., Zhong, S., Zhang, Y., 2009. The Proterozoic VMS copper deposit in Longmen Mountain area of western Sichuan: evidence from sulphide trace element and sulfur isotope. *Geol. Sci. Technol. Inform.* 28, 59–64 (in Chinese with English abstract).
- Yoon, J., Huh, Y., Lee, I., Moon, S., Noh, H., Qin, J., 2008. Weathering processes in the Min Jiang: major elements,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$ , and  $\delta^{18}\text{O}_{\text{SO}_4}$ . *Aquat. Geochem.* 14, 147–170.
- Yu, X., Feng, L., Yan, D., Jia, Y., Yang, S., Hu, D., Zhang, M., 2008. Development of distributed hydrological model for Yalongjiang River basin. *J. China Hydrol.* 28, 49–53 (in Chinese with English abstract).
- Zhang, J., Hu, H., 2000. The research on the CO<sub>2</sub> releasing flux in Xianshuihe fault, Sichuan Province. *Hydrogeol. Eng. Geol.* 3, 19–21 (in Chinese).
- Zhang, J., Quay, P.D., Wilbur, D.O., 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO<sub>2</sub>. *Geochim. Cosmochim. Acta* 59, 107–114.
- Zhu, D., 2007. *China Water System Dictionary*, second ed. Qingdao Press, Qingdao (in Chinese).