

Sulfate sources constrained by sulfur and oxygen isotopic compositions in the upper reaches of the Xijiang River, China

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Abstract While it is critical to accurately understand the sources and transformation of sulfate based on time-series analysis, there are limited studies on temporal variation of sulfate in rivers and on rock weathering by sulfuric acids. We conducted a monthly sampling campaign in the Beipan, Nanpan, and Hongshui Rivers over the course of one hydrological year. This study examined seasonal variations in riverine sulfate impacted by the monsoon climate in the upper reaches of the Xijiang River basin. In general, the SO_4^{2-} contents in these rivers dropped from relatively high levels to low values during the high-flow season, in response to increasing discharge. The sulfate was generally enriched in heavy isotopes during the low-flow season compared to the high-flow season. The calculated results indicate that the riverine sulfate was mainly derived from sulfide oxidation, but that evaporite dissolution could be an important source during the low-flow season, based on isotopic evidence. Mine drainage is likely an important source of sulfate to these rivers during the high-flow season due to contributions from fast surface flow, which responds to frequent heavy rain in monsoonal climate regions. A

relatively high proportion of HCO_3^- was found to be derived from rock weathering by sulfuric acid during the high-flow season when compared to that observed during the low-flow season. The results suggest that approximately one quarter of the HCO_3^- in the Hongshui River originated from carbonate weathering by sulfuric acid derived from the oxidation of sulfide. Such information on the specific dual isotopic characteristics of riverine sulfate throughout a hydrological year can provide unique evidence for understanding the temporal variability of sulfate concentrations and weathering processes in rivers.

Keywords Sulfur isotope · Oxygen isotope · Riverine sulfate · Carbonate weathering · Xijiang River

1 Introduction

Sulfate attracts widespread attention as the dominant form of sulfur in riverine systems. Riverine sulfate generally originates from precipitation and from the weathering of sulfide-bearing minerals and evaporite minerals, as well as from fertilizer and industrial inputs (Yang et al. 1996; Krouse and Mayer 2000; Pawellek et al. 2002; Brenot et al. 2007; Rock and Mayer 2009). There exists a strong linkage between the sulfur cycle and other elemental cycles, such as those of carbon, iron, and nitrogen in the surface environment (Clark and Fritz 1997; Krouse and Mayer 2000; Turchyn and Schrag 2006; Calmels et al. 2007). The temporal and spatial variation of sulfate in river systems can reflect geological characteristics, environmental changes, and anthropogenic inputs (Dogramaci et al. 2001; Jiang et al. 2007). Thus, it is necessary to understand riverine sulfate biogeochemistry in the context of the terrestrial system.

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The sulfur and oxygen isotopes of sulfate are powerful tools for identifying the sources and transformation of sulfate in riverine systems (Clark and Fritz 1997). Sulfate derived from the oxidation of reduced sulfur generally inherits the isotopic composition of the reactants during natural processes. The oxygen isotopic composition of sulfate derived from the oxidation of pyrite depends on the ratio of oxygen sources between the water and atmosphere during different oxidation processes that might be controlled by fractionation processes and environmental conditions (Krouse and Mayer 2000; Kohl and Bao 2011). Riverine SO_4^{2-} originating from the dissolution of evaporite minerals is generally enriched in ^{34}S and ^{18}O . Recent studies have shown that the S and O isotopes are useful indicators of the sources and transformations of sulfate in the rivers (Pawellek et al. 2002; Brenot et al. 2007; Calmels et al. 2007; Rock and Mayer 2009). However, there is limited research focusing on the temporal evolution of sulfate and related C–S coupling using the dual isotope approach in large rivers (Brenot et al. 2007; Rock and Mayer 2009; Li et al. 2015).

The Xijiang River is the main tributary of the Pearl River, and has the second largest discharge in China. Previous studies indicate that sulfate in the Xijiang River may derive primarily from oxidation of sulfide minerals in its upper reaches, based on water chemistry and mixing models (Li et al. 2008; Xu and Liu 2010). However, these studies lack isotopic proof to ascertain sulfate sources and implied carbonate weathering. In this study, water chemistry and sulfate isotopes from the upper reaches of the Xijiang River were investigated based on temporally distributed sampling. The main objective was to evaluate the temporal variations of sulfate, as well as the sources of sulfate and its possible implications for the river.

2 Materials and methods

2.1 Sampling site

The Xijiang River is located between 21°N and 26°N and 102°E and 115°E . Its drainage basin covers 77.8% of the Pearl River's entire drainage basin and provides 63.9% of the Pearl's total discharge. The Xijiang originates in the Maxiong Mountains in Yunnan Province, turns towards the southeast and flows into the South Sea. The length of the Xijiang River is 2075 km. Its drainage basin covers an area of 353,120 km^2 , and it passes through Guizhou, Guangxi, and Guangdong Provinces. The upper reaches of the Xijiang River include the Nanpan, Hongshui, and Beipan Rivers (Fig. 1). As indicated by Fig. 1, this area is widely covered with Permian and Triassic carbonate rocks (limestones and dolomites). The study area also contains detrital

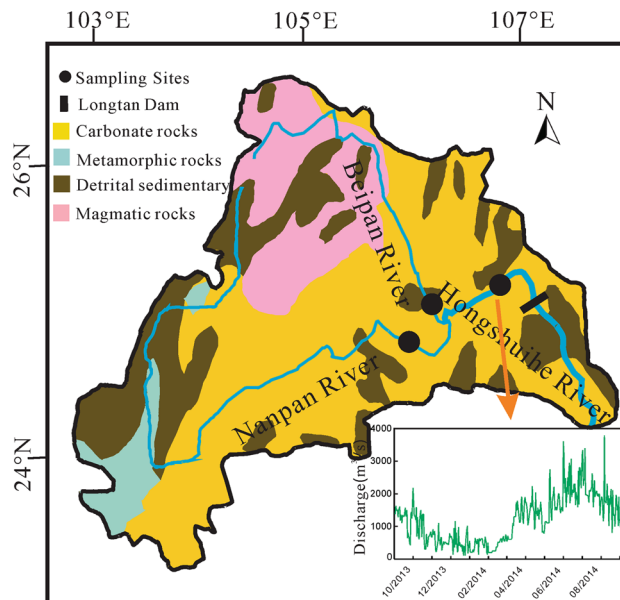


Fig. 1 Sampling locations shown on a geological map of the upper Xijiang River watershed; variation of discharge in the Hongshui River during the sampling period

sedimentary rocks (shales, sandstones, and siltstones) and small amounts of magmatic rocks. There exist sparsely distributed coal and metal mines within the investigated area (Li et al. 2008; Xu and Liu 2010). The landscape of the study area is typified by spectacular karst landforms developed in the carbonate bedrock.

A typical monsoonal climate dominates the whole Xijiang River basin in Southwest China. The seasonal variations of air temperature and discharge are in phase; high discharges occur in summer and low discharges occur winter, owing to the Pacific and Indian Ocean monsoons. Winters are cold and dry with little rainfall, while summers are warm and wet and are accompanied by frequent heavy rain. Annual mean temperature ranges from 14 to 22 $^\circ\text{C}$; annual precipitation ranges from 800 to 1200 mm, with 80% occurring during the rainy season, from April to September. Only two small prefecture-level cities are located within the study area. Agriculture is not developed and related land exhibits a scattered distribution (Liu 2007).

2.2 Sampling and analytical techniques

Water samples were collected monthly over a hydrological year from October 2013 to September 2014 from the Beipan, Nanpan, and Hongshui Rivers. Additional water samples were collected from June to July of 2014 in the Nanpan and Beipan Rivers. Meanwhile, rainwater, chemical fertilizer, and groundwater from the gypsum zone were sampled as endmembers. River water samples were filtered

through 0.45 μm Millipore nitrocellulose membrane filters. Alkalinity was determined by HCl titration. Major cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a precision better than 5%, and anions (Cl^- , SO_4^{2-} , and NO_3^-) were measured by ionic chromatography with a precision of 5%.

Dissolved sulfate was precipitated as BaSO_4 for isotopic measurements by adding BaCl_2 solution to the samples after acidification using HCl. The precipitate was then filtered, washed, and dried. The values of $\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$ were determined using elemental analysis–isotope ratio mass spectrometry (EA-IRMS) and reported using δ notation relative to the Vienna Canyon Diablo Troilite (V-CDT) with a precision better than 0.2‰ and Vienna Standard Mean Ocean Water (V-SMOW) in permil with a precision better than 0.5‰. The measurement of sulfate isotopes was carried out at the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences. The isotope results are given in δ units, which are defined as:

$$\delta(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

where R represents the $^{34}\text{S}/^{32}\text{S}$ or $^{18}\text{O}/^{16}\text{O}$ ratios.

3 Results

3.1 Major ions in the river water

The chemical composition of the water samples from the upper reaches of the Xijiang River was highly variable. The cationic charge ($\text{TZ}^+ = \text{Na}^+ + \text{K}^+ + 2\text{Ca}^{2+} + 2\text{Mg}^{2+}$) varied from 2245 to 4067 $\mu\text{eq/L}$ with an average value of 3459 $\mu\text{eq/L}$, which is 1–3 times greater than the average for the large rivers of the world (1125 μeq) (Meybeck 2003). TZ^- ($\text{HCO}_3^- + \text{Cl}^- + 2\text{SO}_4^{2-} + \text{NO}_3^-$) varied from 2501 to 4255 $\mu\text{eq/L}$, with an average of 3589 $\mu\text{eq/L}$. The normalized inorganic charge balance, $\text{NICB} = (\text{TZ}^+ - \text{TZ}^-)/(\text{TZ}^+ + \text{TZ}^-)$, characterizes the extent of inorganic charge imbalance and generally has values less than $\pm 5\%$. In the upper reaches of the Xijiang River, the ordering of the cation contents was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$, and the Ca^{2+} and Mg^{2+} contributed, on average, 70% and 22% of TZ^+ , respectively. The anion contents followed the order $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$, and the HCO_3^- and SO_4^{2-} contributed, on average, 70% and 22% of TZ^- , respectively.

The concentration of SO_4^{2-} varied from 240 to 752 $\mu\text{mol/L}$ with a mean value of 497 $\mu\text{mol/L}$ for the Beipan River, from 175 to 672 $\mu\text{mol/L}$ with a mean value of 423 $\mu\text{mol/L}$ for the Nanpan River, and from 275 to 679 $\mu\text{mol/L}$ with a mean value of 464 $\mu\text{mol/L}$ for the

Hongshui River. For rainwater samples ($n = 10$) collected from a village in the study area, the concentration of SO_4^{2-} varied from 5 to 27 $\mu\text{mol/L}$ with a mean value of 15 $\mu\text{mol/L}$. For the Hongshui River, the minimum low-flow value occurred in January (110 m^3/s); the maximum high-flow value occurred in September (3769 m^3/s) (Fig. 1). River flow can be roughly divided into two regimes for the purposes of this study: low flow (Oct. 2013 through May 2014) and high flow (Jun. 2014 through Sept. 2014).

3.2 Isotopic compositions of sulfate

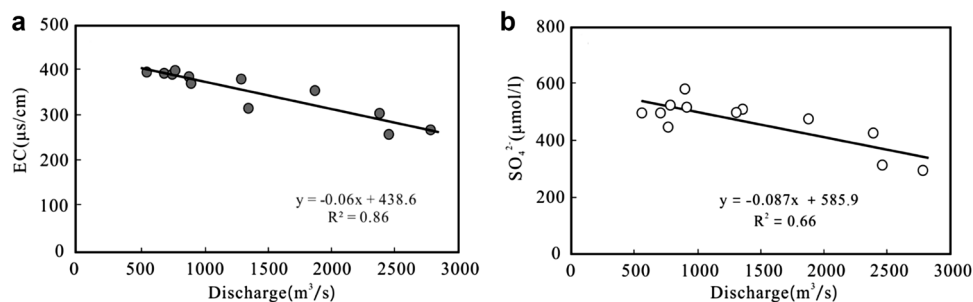
The isotopic compositions of sulfate were found to range from -4.6‰ to 0.5‰ with a median value of -2.1‰ for $\delta^{34}\text{S}\text{-SO}_4^{2-}$ in the sampled rivers; for $\delta^{18}\text{O}\text{-SO}_4^{2-}$, the corresponding range was 3.3‰ – 12.0‰ and the median value 7.0‰ . The mean values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ in the Hongshui River were -1.7‰ and 7.5‰ , which were similar to the median values across the study area. The mean values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ in the Beipan River were -2.6‰ and 7.0‰ , lower than those observed in the Nanpan and Hongshui Rivers. More depleted sulfate $\delta^{18}\text{O}$ values were observed in the water samples collected during the wet season (from Jun. to Sept.) compared with those from the dry season (Feb., Apr., and Nov.). Sulfate from rainwater had $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values of $1.4\text{‰} \pm 0.7\text{‰}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values of $8.9\text{‰} \pm 2.2\text{‰}$. Chemical fertilizer returned $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values of $14.6\text{‰} \pm 2.1\text{‰}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values of $32.9\text{‰} \pm 4.3\text{‰}$. The $\delta^{34}\text{S}$ - and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ of groundwater from the gypsum zone were $25.7\text{‰} \pm 1.5\text{‰}$ and $11.2\text{‰} \pm 1.2\text{‰}$, respectively.

4 Discussion

4.1 Seasonal variations in sulfate and isotopic compositions

In general, there were relatively low contents of the ions Ca^{2+} , HCO_3^- , SO_4^{2-} , Mg^{2+} , and K^+ during the high-flow season compared with the low-flow season in sampled rivers, indicating a dilution effect. There was a clear inverse relationship between discharge and conductivity during the hydrological year in the Hongshui River (Fig. 2a), suggesting that the dissolved load is distinctly impacted by dilution processes. However, NO_3^- and Cl^- did not show negative relationships with discharge in the Hongshui River, indicating complex mixing from various anthropogenic inputs, such as chemical fertilizer, domestic waste, and industrial effluent. Meanwhile, relatively high contents of sulfate were found in some water samples collected from the Beipan River during the high-flow season, which might reflect drought-condition reservoir

Fig. 2 The correlation between discharge and conductivity (a), and sulfate concentration (b), in the Hongshui River



evaporation and substantial inputs from mine drainage and industrial activities, given the coal and metal mines in the study area (Hong et al. 1993; Liu 2007; Li et al. 2008; Yuan 2014). In general, a distinct dilution of sulfate during the high-flow season was evidenced by the inverse relationship between discharge and sulfate, such as that seen in the Hongshui River (Fig. 2b).

In the upper reaches of the Xijiang River, there was a non-significant inverse relationship between the reciprocal of SO_4^{2-} concentration and the values of $\delta^{34}\text{S}\text{-SO}_4^{2-}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ (Fig. 3). A wide range of river water $1/\text{SO}_4^{2-}$ values were measured during the high-flow season, varying from 1.4 to 4.2, and the sulfate was enriched in light sulfur and heavy oxygen isotopes. The $1/\text{SO}_4^{2-}$ values fell within a narrower range, 1.6 to 2.3, during the low-flow season, when the sulfate was enriched in heavy sulfur and oxygen isotopes. However, more negative $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate were observed in the water samples during the high-flow season (from Jun. to Sept.) compared with the low-flow season (Fig. 3). In general, the seasonal variations of isotopic compositions reflected different hydrological conditions. Sulfate originating from mine activities and industrial effluents can be transported through surface flow during the high-flow season. Similar observations have been reported in the Jialing River basin (Li et al. 2011a, b).

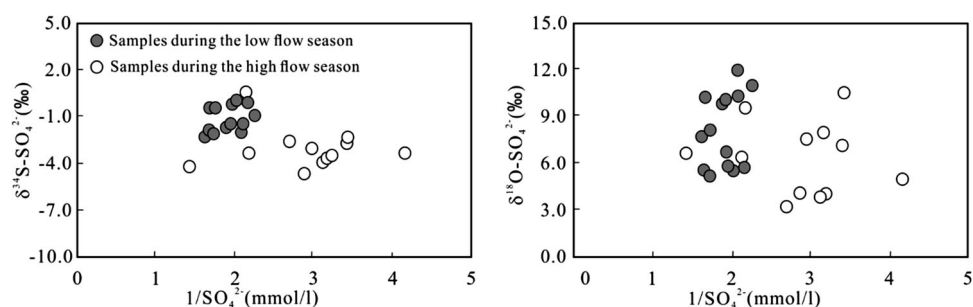
4.2 Sulfate sources constrained by isotopes

The dual isotope approach ($\delta^{34}\text{S}\text{-SO}_4^{2-}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$) presents an opportunity to elucidate the sources and fate of sulfate in various rivers (Calmels et al. 2007; Rock and

Mayer 2009; Turchyn et al. 2013; Li et al. 2014). Distinct isotopic “fingerprint” signatures can be used to characterize different sulfate sources (Krouse and Grinenko 1991), including atmospheric deposition; evaporite dissolution (largely gypsum, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, or anhydrite, CaSO_4); sulfide oxidation (largely pyrite, FeS_2); and anthropogenic inputs, such as chemical fertilizer, domestic waste, industrial effluent, and acid mine drainage (Krouse and Mayer 2000; Brenot et al. 2007; Rock and Mayer 2009). The specific dual isotopic characteristics of riverine sulfate are of unique value in understanding the hydrological year variability of sources in the studied watershed, especially in light of its monsoon climate.

Low pH values and high sulfate contents in rainwater have been found in the industrialized areas of China as a result of anthropogenic activity (Larssen et al. 1999). Southwest China is one of the areas that is most affected by acid rain. The $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values measured in this study from precipitation are characteristic of anthropogenic emissions, especially in industrialized areas. Rainwater samples were collected in situ during the sampling period and had a median value of $30\ \mu\text{mol/L}\ \text{SO}_4^{2-}$, lower than that observed in Guiyang rainwater ($80\ \mu\text{mol/L}\ \text{SO}_4^{2-}$; Han and Liu 2006) or in the studied river water. The isotopic values of sulfate from rain in this study are similar to those from the Sichuan basin (Li et al. 2006), where reported $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values of rainwater ranged from 1.7‰ to 5.6‰ (averaging 3.9‰). It has been reported that the $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values of rainwater ranged from -8.1‰ to -5‰ in Guiyang (Jiang et al. 2007; Liu 2007). The values of $\delta^{18}\text{O}\text{-SO}_4^{2-}$ in atmospheric sulfate generally reflect enrichment in heavy ^{18}O , ranging from 7‰ to 17.2‰ in

Fig. 3 $1/\text{SO}_4^{2-}$ (mmol/L) versus $\delta^{34}\text{S}\text{-SO}_4^{2-}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ in the upper reaches of Xijiang River basin

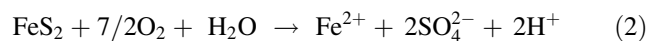


previous studies (Krouse and Mayer 2000; Jenkins and Bao 2006; Brenot et al. 2007), which have also shown that the range of $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values was between 10‰ and 20‰ for atmospheric sulfate. Atmospheric deposition is likely one of the important sources of sulfate in the upper reaches of the Xijiang River based on the frequent acid deposition conditions in the study area (Jiang et al. 2007; Liu 2007) and the $\delta^{34}\text{S}\text{-SO}_4^{2-}$ versus $\delta^{18}\text{O}\text{-SO}_4^{2-}$ diagram (Fig. 4).

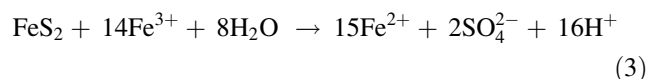
The sulfate derived from evaporite dissolution is typically enriched in heavy sulfur and oxygen isotopes (^{34}S and ^{18}O) and thus plots within the upper right-hand quadrant. It exhibits $\delta^{34}\text{S}_{\text{SO}_4}$ values ranging from 8‰ to 35‰ and $\delta^{18}\text{O}_{\text{SO}_4}$ values ranging from 6‰ to 20‰ (Claypool et al. 1980; Turchyn and Schrag 2006), which typically vary with geological age. The $\delta^{34}\text{S}_{\text{SO}_4}$ values of gypsum deposited during the Late Proterozoic through the Early Cambrian range from 21‰ to 32‰ (Strauss 1997), while $\delta^{18}\text{O}_{\text{SO}_4}$ values range from 10‰ to 20‰ (Turchyn et al. 2013). Sulfate derived mainly from Triassic evaporites yields values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ ranging from 14.5‰ to 32.5‰ and from 13‰ to 15‰, respectively (Strauss 1997; Goldberg et al. 2005). Within the study area, we collected water samples that inherited evaporite isotopic characteristics. The isotopic values of sulfate were higher than those from the river waters; in particular, the $\delta^{34}\text{S}\text{-SO}_4^{2-}$ values were above +20‰.

Shale and sulfide minerals are widely distributed in the investigated catchment; thus, sulfide oxidation could be an important source of sulfate contributions to the Xijiang River. In a previous study, $\delta^{34}\text{S}$ values mainly ranged from -27‰ to 15‰ for sulfide minerals situated in southwest Guizhou Province (Yuan 2014). In general, sulfate derived from oxidation of sulfide in Guizhou Province has $\delta^{34}\text{S}$ values ranging from 5‰ to 10‰ (Liu 2007). Coal has $\delta^{34}\text{S}$ values that mainly range from -7‰ to 5‰ in Guizhou Province (Hong et al. 1993). Coal mines are widely

distributed in the Beipan and Nanpan River basins. Mine drainage in Guizhou Province, has $\delta^{34}\text{S}$ values close to -13‰ (Jiang et al. 2007). In general, $\delta^{34}\text{S}\text{-SO}_4^{2-}$ generally inherits the isotopic composition of the reduced sulfur (Krouse and Mayer 2000; Liu 2007), while the ratio of oxygen between atmosphere and water in sulfate during pyrite oxidation might depend on the various oxidation pathways and environmental conditions (Kohl and Bao 2011). In general, two main sulfide oxidation processes are present under natural conditions (Taylor et al. 1984; van Everdingen and Krouse 1985; van Stempvoort and Krouse 1994). The first major reaction of pyrite oxidation is as follows:



where 7/8 of the oxygen in the sulfate is contributed by molecular atmospheric oxygen, while the remaining 1/8 oxygen comes from water. The resulting sulfate is enriched in the heavy sulfur isotope (^{34}S) and the light oxygen isotope (^{16}O). The second reaction is the oxidation of pyrite by ferric iron:



where the oxygen in the sulfate is derived exclusively from water. Compared to Reaction 2, ferric iron can rapidly oxidize pyrite under anaerobic and abiotic conditions via Reaction 3, respectively. Either Reactions 2 or 3 may dominate, which demonstrates the complexity of oxygen sources in riverine sulfate. In addition to the two primary oxygen sources, the $\delta^{18}\text{O}$ value of sulfate is influenced by isotopic fractionation effects. According to the second equation (van Everdingen and Krouse 1985; van Stempvoort and Krouse 1994), we could calculate the $\delta^{18}\text{O}$ of dissolved sulfate using the fraction of O_2 versus H_2O and their respective enrichment factors. The large contrast in the oxygen isotopic composition between the atmosphere and meteoric water can potentially allow identification of pyrite oxidation pathways. The isotopic compositions of atmospheric oxygen and meteoric water are approximately 23.5‰ and <0‰, respectively (Kroopnick and Craig 1972). The enrichment factors of $\varepsilon^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$ and $\varepsilon^{18}\text{O}_{\text{SO}_4\text{-O}_2}$ can be assigned values of 4.1‰ and -11.4‰ (Taylor et al. 1984; van Everdingen and Krouse 1985; van Stempvoort and Krouse 1994). Within the study area, the $\delta^{18}\text{O}\text{-H}_2\text{O}$ in river waters ranges approximately from -10‰ to -8‰ (Li et al. 2015); therefore, the $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values would be -5‰ to 9‰. Of course, there are the above-mentioned uncertainties of oxygen isotopic composition during sulfide oxidation. In general, sulfate derived from the oxidation of coal is enriched in the heavy isotopes of oxygen, due to oxidation by oxygen. However, sulfate

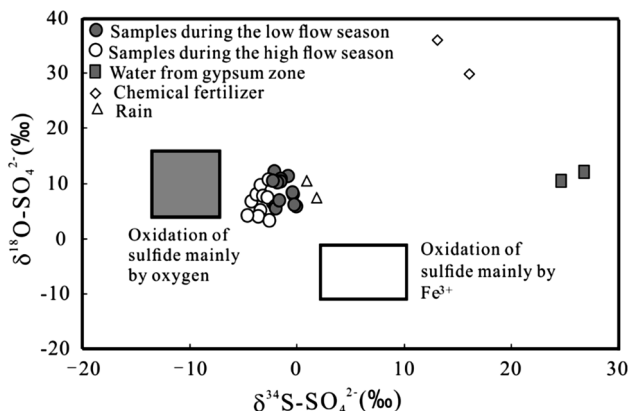


Fig. 4 $\delta^{34}\text{S}\text{-SO}_4^{2-}$ versus $\delta^{18}\text{O}\text{-SO}_4^{2-}$ in the upper reaches of the Xijiang River basin

derived from oxidation of sulfide minerals by iron is enriched in the light oxygen isotope. Meanwhile, sulfate derived from the dissolution of gypsum generally has $\delta^{18}\text{O-SO}_4^{2-}$ values above +10‰ (Turchyn and Schrag 2006), suggesting that oxidation of reduced sulfur compounds is a major source of riverine sulfate in the present study. Jiang et al. (2007) and Li et al. (2011a, b) described similar observations in the Wujiang and Jialingjiang Rivers, respectively, and proved that most riverine sulfate derived from sulfide oxidation.

The values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for sulfate of anthropogenic origin range from 0‰ to 10‰ and from 5‰ to 20‰, respectively (Longinelli and Cortecchi 1970; Krouse and Grinenko 1991; Jádrysek 2000). The $\delta^{34}\text{S}$ values of domestic detergents widely used in homes in the Sichuan Basin range from 15.2‰ to 17.2‰ (Li et al. 2006), while in Spain these values range from 8.5‰ to 13.6‰ (Vitòria et al. 2004). The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of fertilizers widely used in Spain range from –6.5‰ to +21.4‰ and from 7.7‰ to +16.5‰, respectively (Vitòria et al. 2004). Chemical fertilizers have relatively high $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{18}\text{O-SO}_4^{2-}$ values, which are far above those observed in river waters. Thus, the contribution of chemical fertilizers appears to be of minor importance for riverine sulfate.

The sulfur and oxygen isotopic compositions of sulfate in the upper reaches of the Xijiang River suggest at least four endmembers—atmospheric deposition, oxidation of reduced sulfur, evaporite dissolution, and anthropogenic inputs (Fig. 4). As indicated by Fig. 4, oxidation of reduced sulfur should be a major source of sulfate for these rivers. The riverine SO_4^{2-} was characterized by relatively high values of $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{18}\text{O-SO}_4^{2-}$ during the low-flow season, indicating that more sulfate originated from evaporite dissolution at that time than during the high-flow season. Sulfate was characterized by relatively low $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{18}\text{O-SO}_4^{2-}$ values during the high-flow season, suggesting greater contributions from sulfide oxidation and atmospheric deposition. More sulfate derived from the oxidation of sulfide from mines and soil is transported via surface flow into rivers during the high-flow season, which might account for shifts in isotopic values and seasonal variability of sulfate in the rivers. A similar pattern—lower $\delta^{34}\text{S-SO}_4^{2-}$ values and higher $\delta^{18}\text{O-SO}_4^{2-}$ values in the rainy season—was reported in the Yangtze River (Li et al. 2011b).

4.3 Calculated contributions from different sulfate sources

The various riverine sulfate sources can be quantified based on the above discussion of potential sources of sulfate to the upper reaches of the Xijiang River. Potential contributions from chemical fertilizers were ignored in this study, due to

the large differences in isotopic compositions between fertilizer and the sulfate in the river. Additionally, sulfate is not a major component of most chemical fertilizers. The chemical characteristics of the river water samples of the Hongshui River were used in our calculations. We assigned $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{18}\text{O-SO}_4^{2-}$ values of 1.4‰ and 8.9‰ for rainwater, –13.0‰ and 9.0‰ for the oxidation of coal, 8.0‰ and –2.0‰ for the oxidation of sulfide, and 25.7‰ and 11.2‰ for evaporite dissolution, respectively. The rainwater from villages in the study area contained small amounts of sulfate, with a median value of 30 $\mu\text{mol/L}$. This concentration is lower than the 90 $\mu\text{mol/L}$ observed in rainwater of urban areas in southwestern China (Jiang et al. 2007). Here, we assigned the atmospheric source of sulfate a concentration of 60 $\mu\text{mol/L}$ after consideration of the evaporation effect and of the limited rainwater samples collected in the studied area. Thus, the contribution of sulfate to the river from rainwater ranged from 8% to 34% in these rivers. The contributions from different endmembers were calculated as follows (Li et al. 2014):

$$[\text{SO}_4] = [\text{SO}_4]_{\text{atm}} + [\text{SO}_4]_{\text{sulfide}} + [\text{SO}_4]_{\text{evap}} \quad (4)$$

$$\delta^{34}\text{S}_{\text{river}}^* = \delta^{34}\text{S}_{\text{sulfide}} \times (a + b) + \delta^{34}\text{S}_{\text{evap}} \times (1 - a - b) \quad (5)$$

$$\delta^{18}\text{O}_{\text{river}}^* = \delta^{18}\text{O}_{\text{sulfide}} \times (a + b) + \delta^{18}\text{O}_{\text{evap}} \times (1 - a - b) \quad (6)$$

where $(a + b)$ is the proportion of the total sulfate derived from oxidation of sulfide with different isotopic characteristics. $\delta^{34}\text{S}_{\text{river}}^*$ and $\delta^{18}\text{O}_{\text{river}}^*$ represent isotopic values of sulfate after correction for rain input. Water flux in the high-flow and low-flow seasons make up 80% and 20% of the total flux, respectively, in the upper reaches of the Xijiang River (the mean annual runoff is $687 \times 10^8 \text{ m}^3$; Pearl River Water Resources Commission of the Ministry of Water Resources, <http://www.pearlwater.gov.cn/>). The calculations show that in the Hongshui River—in the upper reaches of the Xijiang River—sulfide oxidation contributed 65% of the sulfate in the low-flow season and 80% in the high-flow season; rainwater contributed 12%–15% of the sulfate to the Hongshui River. On the other hand, evaporite dissolution became increasingly significant during the low-flow season. The calculated data are consistent with the above discussion of changes in the various sources of riverine sulfate between the two seasons in the upper reaches of the Xijiang River. Of course, the calculated results might over- or underestimate the contribution from oxidation of sulfide and gypsum since we ignored anthropogenic sources in the calculations, due to their assumed relatively minor contribution. Ultimately, the calculated contribution of sulfate from the oxidation of sulfide in the Hongshui River is in agreement with previous studies in

Spence and Telmer (2005); Calmels et al. (2007) and Li et al. (2011a, b, 2014). These studies suggest that high proportions of sulfate are derived from the oxidation of sulfide in various riverine systems.

4.4 Implications for the carbonate weathering budget

Previous studies have suggested that sulfuric acid is an important weathering agent for rock weathering in various basins, due to the wide distribution of sulfide minerals over the Earth's surface (Spence and Telmer 2005; Calmels et al. 2007; Li et al. 2008, 2011a, b, 2014). Oxidation of sulfide minerals produces acid, and the acid reacts with rock, especially carbonates. Hong et al. (1993) showed that large amounts of sulfides are present in the coal strata interbedded with carbonates in South China. In such a system, reactions between sulfuric acid and carbonate rock should occur widely. In this study, approximately 77% of the sulfate was derived from the oxidation of sulfide, which suggests that a large amount of acid is produced in the upper reaches of the Xijiang River. However, the acid would be neutralized by carbonate rock and produce alkalinity for rivers. In this study, carbonate weathering accounted for approximately 23% of HCO_3^- during the low-flow season and 26% of HCO_3^- during the high-flow season, with negligible silicate weathering by sulfuric acid. These proportions are higher than those in the Yalong River (Li et al. 2014) and lower than those in the Beipan River (Li et al. 2008). The calculated proportion has some uncertainties due to dissimilarities among the assigned endmembers, uncertainties in the anthropogenic input, the neglect of biological processes, and errors introduced through multiple computations. Nonetheless, the large amount of HCO_3^- produced by the reaction of carbonate rock and sulfuric acid should be considered carefully in the context of regional and global carbon cycling.

5 Conclusions

In this study, sources and seasonal variations of sulfate were identified using stable isotopic analysis of samples collected monthly in the Beipan, Nanpan, and Hongshui Rivers over the course of a hydrological year. We examined the effects of seasonal variations (impacted by the monsoon climate) on the sulfate sources of the upper reaches of the Xijiang River. The distinct seasonal variations in sulfate in the rivers showed lower SO_4^{2-} contents during the high-flow season, suggesting a dilution effect. In general, the sulfate was generally enriched in light isotopes during the high-flow season compared to the low-flow season, which might reflect anthropogenic inputs, such as

mine drainage that follows fast surface flow in response to the frequent heavy rains in the study area. The calculated results indicate that the riverine sulfate was mainly derived from sulfide oxidation, whereas evaporation dissolution could have been important during the low-flow season, based on the isotopic evidence. The results further suggest that a large amount of sulfate in the Hongshui River was derived from sulfide oxidation, including 65% in the low-flow season and 80% in the high-flow season. Approximately 23% of the HCO_3^- in the low-flow season and 26% of the HCO_3^- in the high-flow season originated from carbonate weathering by sulfuric acid. This suggests that carbonate weathering by sulfuric acid should be incorporated into the carbon budget of this riverine system. In sum, information on the dual isotopic characteristics of riverine sulfate can be uniquely helpful in understanding seasonal variability in sulfate sources and weathering processes in these rivers.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interests.

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