



## Seasonal changes in the radiogenic and stable strontium isotopic composition of Xijiang River water: Implications for chemical weathering

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### ABSTRACT

Seasonal changes in strontium (Sr) isotopic systematics in large rivers can effectively track temporal variations in regional chemical weathering, and help to better constrain the Sr isotopic budget of global oceans. However, such records are scarce. Here we present a year-long time-series of both radiogenic and stable Sr isotope measurements ( $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88}\text{Sr}$ ) from river water at Guiping, in the middle reaches of the Xijiang River, South China. Temporal changes in chemical weathering in the drainage basin were investigated by recording seasonal changes in the composition of both Sr isotopes and major ions in the river water. River water  $^{87}\text{Sr}/^{86}\text{Sr}$  values range from 0.708487 to 0.710336, with most values being  $<0.7092$ , indicating a dominant contribution from the weathering of carbonate rocks. High  $^{87}\text{Sr}/^{86}\text{Sr}$  values ( $>0.7092$ ) are generally accompanied by high Rb/Sr ratios, and low pH and  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) and occur during periods of large river flux. This indicates that the contribution to the chemistry of river water from the weathering of silicate rocks is enhanced during rainy seasons. Seasonal variation in river water  $\delta^{88}\text{Sr}$  is large, from 0.147‰ to 0.661‰, with higher  $\delta^{88}\text{Sr}$  values generally corresponding to higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values. Again, low  $\delta^{88}\text{Sr}$  values ( $<0.3\text{‰}$ ) suggest a dominant contribution from the weathering of carbonate rocks, whereas the high  $\delta^{88}\text{Sr}$  values may represent a contribution from intensive weathering of silicate rocks. Using the time-series data, we estimated the flux-weighted averages of Sr concentration,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\delta^{88}\text{Sr}$  for the Xijiang River to be 1.00  $\mu\text{mol/L}$ , 0.70960, and 0.38‰, respectively. The Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  results are close to previous estimates, while the  $\delta^{88}\text{Sr}$  value is amongst the highest recorded for the large rivers of the world, and is close to that of seawater. Our results indicate that large rivers draining through tropical/sub-tropical regions could play an important role in regulating the stable Sr isotopic budget of global oceans.

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### 1. Introduction

Studying strontium isotopic systematics in river water has great potential for understanding continental chemical weathering, an important sink for atmosphere  $\text{CO}_2$  over geological history. The flux of dissolved Sr in large rivers, as well as the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, plays an important role in regulating the Sr isotope composition of global oceans (Palmer and Edmond, 1989), with increasing oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$  values generally indicating enhanced weathering of silicate rock on the continents (Brass, 1976; Burke et al., 1982; Richter et al., 1992). Radiogenic Sr isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) can be used to determine the relative contribution to  $\text{CO}_2$  consumption of the weathering of silicate and carbonate rocks (Krishnaswami et al., 1992; Palmer and Edmond, 1992; Negrel et al., 1993; Pande et al., 1994), because dissolved Sr sourced from the

weathering of carbonate rocks generally has higher Sr concentrations and lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values, while that sourced from the weathering of silicate rocks has lower Sr concentrations and higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Krishnaswami et al., 1992). This is particularly important for a more precise estimate of atmospheric  $\text{CO}_2$  consumption by continental chemical weathering (Bernier et al., 1983; Amiotte-Suchet and Probst, 1995; Gaillardet et al., 1999). However, studies of Himalayan rivers indicate that weathering of the trace amounts of disseminated calcite found in silicate rocks, which may have formed during metamorphism and interaction with Rb-rich silicate rocks (Bickle et al., 2001), may also yield dissolved Sr with extremely high  $^{87}\text{Sr}/^{86}\text{Sr}$  values (up to 0.8) (Blum et al., 1998; Jacobson and Blum, 2000). Thus, high  $^{87}\text{Sr}/^{86}\text{Sr}$  values of dissolved Sr in river water may not necessarily indicate enhanced weathering of silicate rocks (Palmer and Edmond, 1992; Blum et al., 1998; Jacobson and Blum, 2000). This has led to an ongoing debate on the relative contribution to  $\text{CO}_2$  consumption of the weathering of carbonate and silicate rocks as estimated from  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Harris et

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al., 1998; Singh et al., 1998; Galy et al., 1999; Dalai et al., 2003; Quade et al., 2003; Bickle et al., 2005), and a more reliable estimate needs multiple constrain by coupling with other data, such as the composition of the major ions (Bickle et al., 2005).

In addition to the radiogenic Sr isotopic ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), the stable Sr isotopic ratio,  $^{88}\text{Sr}/^{86}\text{Sr}$ , has been increasingly employed in recent years to indicate variations of Sr isotopes. The  $\delta^{88}\text{Sr}$  (or  $\delta^{88/86}\text{Sr}$ ), defined as  $\delta^{88}\text{Sr} = 1000 \times (^{88}\text{Sr}/^{86}\text{Sr}_{\text{sample}} / ^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}} - 1)$ , is adopted to describe changes in  $^{88}\text{Sr}/^{86}\text{Sr}$  (Fietzke and Eisenhauer, 2006).  $^{88}\text{Sr}/^{86}\text{Sr}$  has generally been considered as constant ( $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$ ; Nier, 1938), and has been used for mass bias correction during Sr isotope measurements. Some recent studies, however, indicate variable  $^{88}\text{Sr}/^{86}\text{Sr}$  values in different geological bodies. Seawater appears to be homogeneous and has high  $\delta^{88}\text{Sr}$  values of  $\sim 0.38\%$  to  $0.39\%$  (Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Ohno et al., 2008; Krabbenhoft et al., 2010); marine biogenic carbonates show values from  $0.1\%$  to  $0.3\%$  (Halicz et al., 2008; Ohno et al., 2008; Krabbenhoft et al., 2010);  $\delta^{88}\text{Sr}$  in terrestrial silicate rocks generally ranges from  $0.2\%$  to  $0.3\%$  (Moynier et al., 2010; Charlier et al., 2012); and terrestrial carbonates show very negative values of  $\sim -0.1\%$  to  $-0.3\%$  (Halicz et al., 2008; Ohno et al., 2008). Chemical weathering, pedogenesis, and carbonate deposition are likely the main processes that cause the fractionation of stable Sr isotopes (Halicz et al., 2008).

Similar to that for  $^{87}\text{Sr}/^{86}\text{Sr}$  values, the  $\delta^{88}\text{Sr}$  value of dissolved Sr in river water may also provide a means of tracking continental chemical weathering, leading to a better understanding of Sr stable isotope budgets in the oceans (Krabbenhoft et al., 2010). As both  $^{88}\text{Sr}$  and  $^{86}\text{Sr}$  are not radiogenic isotopes,  $\delta^{88}\text{Sr}$  values will remain constant through geological history, while  $^{87}\text{Sr}/^{86}\text{Sr}$  may change due to the accumulation of radiogenic  $^{87}\text{Sr}$  decayed from  $^{87}\text{Rb}$ . It appears the problem of disseminated calcite sourced from weathering, which produces high  $^{87}\text{Sr}/^{86}\text{Sr}$  in the Himalayan rivers (Blum et al., 1998; Jacobson and Blum, 2000), may not be relevant to  $\delta^{88}\text{Sr}$  studies. Therefore, coupled radiogenic and stable Sr isotopes may potentially provide better constraints on the contribution from weathering of carbonate and silicate rocks, and help to better constrain estimates of the consumption of atmosphere  $\text{CO}_2$  by chemical weathering. However, few studies have examined stable Sr isotopes in large rivers, and the amount of available  $\delta^{88}\text{Sr}$  data is limited. Thus, little is known about the variation of  $\delta^{88}\text{Sr}$  in river water and how these variations may link to continental chemical weathering.

de Souza et al. (2010) suggested that Sr released during incipient chemical weathering of silicate rocks shows no significant  $\delta^{88}\text{Sr}$  difference from that in the parent rocks. However, the  $\delta^{88}\text{Sr}$  values of the dissolved Sr in some relatively large rivers are  $>0.3\%$ . For example, the  $\delta^{88}\text{Sr}$  of the Yangtze River, the largest river in China, is  $\sim 0.38\%$ , which is similar to that of seawater (Krabbenhoft et al., 2010). This value is significantly higher than those reported from most carbonate and silicate rocks (Halicz et al., 2008; Ohno et al., 2008; Moynier et al., 2010; Charlier et al., 2012). Thus, there may be some processes that cause fractionation of stable Sr isotopes during chemical weathering. How do varying contributions of dissolved Sr from the weathering of either carbonate or silicate rocks affect  $\delta^{88}\text{Sr}$  values, and which processes may cause stable Sr isotope fractionation during chemical weathering? Answering these questions is important to further our understanding of the linkages between stable Sr isotopes and chemical weathering.

Another factor that may influence both the radiogenic and stable Sr isotopes values in river water is seasonal changes in chemical weathering. In regions where seasonal variations of temperature and precipitation are large, such as monsoonal regions, the rate of chemical weathering may change throughout the year, which may subsequently result in seasonal changes in the Sr isotope composition of the river water (Bickle et al., 2003). Studies in Himalayan rivers indicate a decline in silicate weathering during the monsoon season, as indicated by lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values in river water (Rai and Singh, 2007; Tripathy et al., 2010). Such seasonal  $^{87}\text{Sr}/^{86}\text{Sr}$  variations are up to  $\sim 20\%$  to  $30\%$  (Bickle et al., 2003; Rai and Singh, 2007; Tripathy et al., 2010). If this phenomenon is not

considered, the seasonal flux of Sr isotopes, as estimated using only rainy or dry season data, may deviate significantly from the true values (Tripathy et al., 2010). As for many other regions, the reasons for seasonal changes are largely unknown, and more studies are needed to evaluate the possible influence of seasonal changes on Sr isotope budgets.

Herein, we present a year-long time-series of both radiogenic and stable Sr isotopes of the Xijiang River, the main channel of the Pearl River, South China. In addition to variations in major anions, and major and trace element compositions, seasonal variations of chemical weathering in the drainage basin are discussed. This study is the first to show seasonal variations in stable Sr isotope compositions for dissolved Sr in large rivers. The results will aid our understanding of stable Sr isotope fractionation during chemical weathering, and will lead to a better understand of chemical weathering in tropical regions affected by monsoon climates.

## 2. Study area

The Xijiang River is the main channel of the Pearl River, the second largest river in China in terms of discharge. The climate of the Xijiang River basin is typical of tropical/subtropical monsoonal regions, with mean annual temperatures ranging from  $14\text{ }^\circ\text{C}$  to  $23\text{ }^\circ\text{C}$ . The annual precipitation ranges from 1000 to 2000 mm, with most of the precipitation occurring in the rainy season from April to September. Carbonate rocks, mainly limestone, dominate the drainage basin, in particular in the upper and the middle reaches of the Xijiang River (Gao et al., 2009) (Fig. 1). Chemical weathering of carbonate rocks is the main contributor to the chemistry of the Xijiang River water, although the weathering of silicate rocks also makes a contribution (Xu and Liu, 2007; Li et al., 2008; Gao et al., 2009; Wei et al., 2011). Chemical weathering in the region is performed not only by atmospheric  $\text{CO}_2$ , but also by sulfuric acid from coal-combustion, and oxidation of sulfide minerals during weathering of coal-containing strata and coal mining (Xu and Liu, 2007; Li et al., 2008).

Guiping, located in the middle reaches of the Xijiang River, was selected for investigation during this study. The mean annual temperature and precipitation in Guiping are  $\sim 22\text{ }^\circ\text{C}$  and  $\sim 1700\text{ mm}$ , respectively. The largest tributary, the Yujiang River, joins the main stream of the Xijiang River at the city of Guiping, where a large dam has been constructed across the tributary (Fig. 1). To diminish the impact of human activity on the study, the observation station ( $23^\circ 24' 47.12''\text{N}$ ,  $110^\circ 4' 12.88''\text{E}$ ) is located at the main channel of the Xijiang River, before the river passes through Guiping city and before the Yujiang River joins the Xijiang River. Seasonal changes in river flux at the observation station are significant, with the maximum flux generally being  $> 5000\text{ m}^3/\text{s}$  during the main rainy season in June.

## 3. Materials and methods

Water sampling was carried out during weekend mornings, once a week from July 2009 to August, 2010. Temperature, pH, and conductivity were measured in the field using a Thermo Orion 4-star Plus pH/conductivity meter. River water samples intended for analysis of the  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) were filtered in the field through  $0.45\text{ }\mu\text{m}$  Millipore membrane filters, and immediately sealed in 40-mL glass bottles with septa closures (CNW Technologies GmbH). To aid preservation,  $\text{HgCl}_2$  was added prior to sealing and the bottles were tightly capped with no head space. River water for other measurements was collected in 10 L brown glass bottles, and filtered through  $0.45\text{ }\mu\text{m}$  Millipore membrane filters once returned to the laboratory. Samples for cations, trace elements, and Sr isotope measurements were acidified with concentrated  $\text{HNO}_3$  and stored in polyethylene plastic (PP) bottles, while samples for anion measurements were directly sealed in PP bottles without acid treatment.

The composition of the anions, and major and trace elements of the water samples have previously been reported by Wei et al. (2011). The

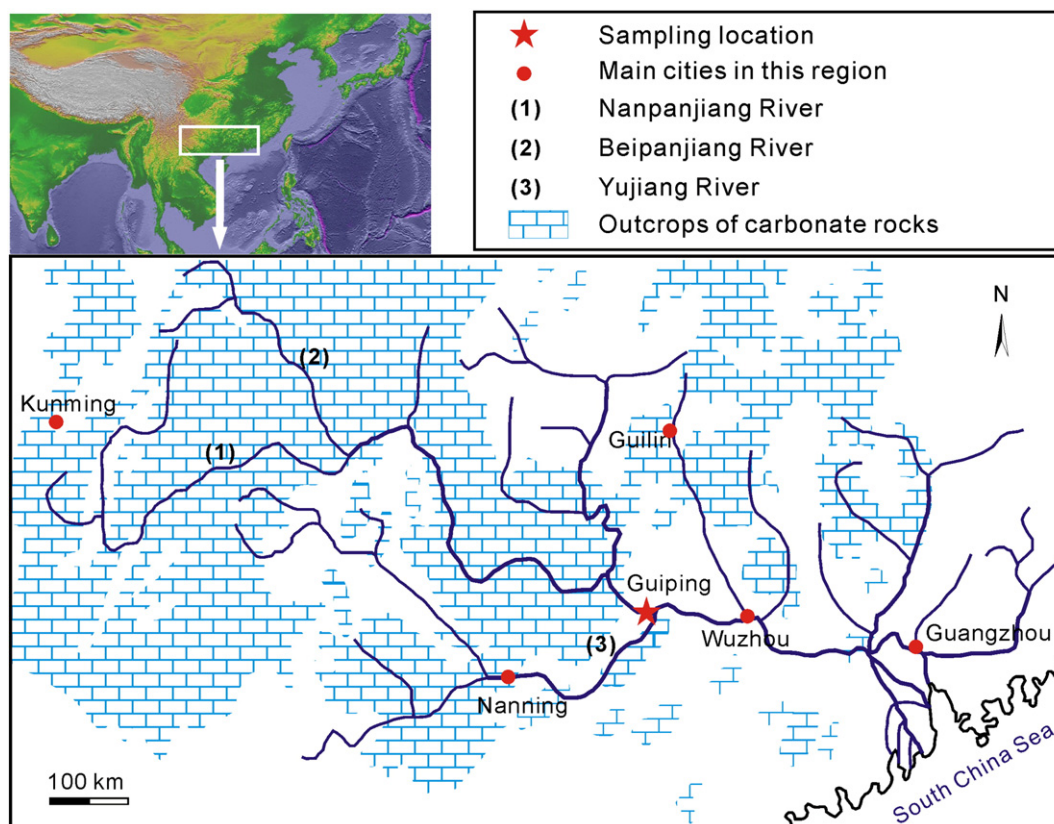


Fig. 1. Map showing the course of the Xijiang River and the location of Guiping and other main cities. Inset shows the location of the Xijiang River drainage basin.

anions were measured using a Dionex ICS-900 ionic chromatography, while the major and trace elements were measured using a Thermo Element II inductively coupled plasma–mass spectrometer (ICP–MS) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China. The precision for the major and trace elements, and anion measurements is generally better than 5% (RSD: relative standard deviation). For details of the measurements refer to Wei et al. (2011).

The DIC  $\delta^{13}\text{C}$  of the samples was measured using a GV Isoprime 100 Isotope Ratio Mass Spectrometer (IRMS) coupled with an online water/gas preparation system (MultiFlow®) at the same laboratory. Approximately 0.5 mL of river water was injected into a sealed bottle using a syringe, which had been pre-flushed with He gas. Subsequently, three drops of 104%  $\text{H}_3\text{PO}_4$  were added to react with the water, and left to stand for 4 h at 40 °C. The liberated  $\text{CO}_2$  was then carried to the IRMS by He gas flow for C–O isotopic analyses. Carbon isotopes are expressed as  $\delta^{13}\text{C}$  relative to the Vienna PDB standard by calibrating the reference  $\text{CO}_2$  gas with several international carbonate standards, such as NBS-19 and IAEA CO-1. A  $\text{NaHCO}_3$  working standard solution was repeatedly measured with the samples, yielding a precision of better than  $\pm 0.1\%$  for  $\delta^{13}\text{C}$ .

A subset of the samples collected from July 2008 to August 2009 was selected for Sr isotope measurements. The Sr concentration of the samples varied from 0.75 to 2.07  $\mu\text{mol/L}$  (Wei et al., 2011). About 5 mL of samples was transferred to pre-cleaned 7 mL PFA beakers, dried on hot plates, and then re-dissolved in 2 mL 4 M  $\text{HNO}_3$ . The purification of Sr was carried out by ion chromatography using Eichrom Sr Resin (50–100 mesh). Each new 0.3 g Eichrom Sr Resin was loaded into an Eichrom 2 mL polypropylene column with an inner diameter of 0.8 cm. The resin was first washed with 15 mL 4 M  $\text{HNO}_3$ , then rinsed with 15 mL milli-Q water, and finally balanced by the addition of 3 mL 4 M  $\text{HNO}_3$ . Samples were re-dissolved in 2 mL 4 M  $\text{HNO}_3$  before being loaded onto the prepared column. The matrix was removed by rinsing with 20 mL 4 M  $\text{HNO}_3$ . The purified Sr was eluted and collected using 8 mL milli-Q water, to ensure that all the Sr was recovered. All the

chemical treatments were performed in the clean lab of the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The milli-Q water was prepared using the Millipore® system yielding a resistivity of 18.2  $\text{M}\Omega\cdot\text{cm}$ . All acids were purified from ultrapure grade reagents by DST-1000 sub-boiling, purchased from the Savillex Corporation, USA. The Sr blank of the total chemical treatment was less than 1 ng. As the amount of Sr in each of our measured 5 mL water samples is on the order of ~300 to 1000 ng, the influence of <1 ng analytical blank is negligible.

The  $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  of the purified Sr samples were measured on a Thermo Neptune multi-collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) from the same laboratory, using the sample standard bracketing (SSB) mode similar to that used by Fietzke and Eisenhauer (2006). During analysis, each sample was bracketed both before and after with measurement of the standard SRM 987. All the SRM 987 standards and the samples were adjusted to the concentration of ~50  $\mu\text{g/L}$ . This concentration yielded an  $^{88}\text{Sr}$  intensity of  $\sim 8 \pm 0.5$  V, with an instrument  $^{88}\text{Sr}$  background generally less than 0.5 mV. The interferences of  $^{86}\text{Kr}$  on  $^{86}\text{Sr}$  and  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$  were monitored by measuring  $^{83}\text{Kr}$  and  $^{85}\text{Rb}$ , and corrected by using  $^{86}\text{Kr} = 1.50566 \times ^{83}\text{Kr}$ , and  $^{87}\text{Rb} = 0.3857 \times ^{85}\text{Rb}$ , respectively. Each measurement was taken in 10 blocks, and each block contained 10 cycles. Both the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{88}\text{Sr}/^{86}\text{Sr}$  ratios without internal correction for mass bias by  $^{88}\text{Sr}/^{86}\text{Sr}$  were collected, and the traditional  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was also calculated by internally calibrating with  $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$  using an exponent law for each sample. The  $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}^*$  values of the samples were calculated as follows:

$$\delta^{88}\text{Sr} = \left( \frac{2 \times ^{88}\text{Sr}/^{86}\text{Sr}_{\text{Sample}}}{^{88}\text{Sr}/^{86}\text{Sr}_{\text{NBS987B}} + ^{88}\text{Sr}/^{86}\text{Sr}_{\text{NBS987A}}} - 1 \right) \times 1000$$

$$^{87}\text{Sr}/^{86}\text{Sr}^* = \frac{2 \times 0.710250 \times ^{87}\text{Sr}/^{86}\text{Sr}_{\text{Sample}}}{^{87}\text{Sr}/^{86}\text{Sr}_{\text{NBS987B}} + ^{87}\text{Sr}/^{86}\text{Sr}_{\text{NBS987A}}}$$

where NBS987B and NBS987A refer to the standard measured before and after the sample, respectively. The errors for the measured  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  were generally  $\pm 5\text{--}8 \times 10^{-5}$  (2SEM: two standard error of the mean) and  $\pm 4\text{--}7 \times 10^{-6}$  (2SEM), respectively. The errors for the  $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}^*$  values of the samples can thus be calculated by using the errors of the measured ratios, both of the sample and of the bracketed SRM 987 standards, using a Gaussian error transport equation. This provides an internal precision (2SEM) of  $\pm 0.007$  to  $\pm 0.012$  for  $\delta^{88}\text{Sr}$ , and  $\pm 8 \times 10^{-6}$  to  $\pm 12 \times 10^{-6}$  for  $^{87}\text{Sr}/^{86}\text{Sr}^*$ . This  $^{87}\text{Sr}/^{86}\text{Sr}^*$  is different from the traditional  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained by internally correcting mass bias using  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ ; it is free from the influence of changing  $^{88}\text{Sr}/^{86}\text{Sr}$  in the samples, and corresponds to the  $^{87}\text{Sr}/^{86}\text{Sr}^*$  value obtained using the methods of Krabbenhoft et al. (2009), Liu et al. (2012), and Yang et al. (2008). The international seawater standard, IAPSO, was repeatedly chemically treated and measured with the samples, yielding the values of  $0.402 \pm 0.012$  (1SD: one standard deviation),  $0.709319 \pm 12$  (1SD), and  $0.709177 \pm 13$  (1SD) ( $n = 10$ ) for  $\delta^{88}\text{Sr}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}^*$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$ , respectively. These values are within analytical error of those obtained by using the double spike–thermal ionization mass spectrometry (DS-TIMS) method of Krabbenhoft et al. (2009), which are 0.386, 0.709312, and 0.709173, respectively. The Sr isotope measurements, together with the related data for anions, and major and trace elements, are listed in Table 1.

#### 4. Results

The river water fluxes at Guiping vary significantly, from  $150 \text{ m}^3/\text{s}$  during winter to  $14,700 \text{ m}^3/\text{s}$  during the flood period of June 2010. The total dissolved solid (TDS) content of the river water varied from 87 to 163 mg/L, while the pH varied from 7.808 to 8.754, with low pH values generally corresponding to large fluxes during flood periods.  $\text{Ca}^{2+}$  is the major cation in the river water, accounting for over 75% of the total cations, with concentrations ranging from 799 to 1315  $\mu\text{mol/L}$ .  $\text{Mg}^{2+}$  is the second most abundant cation, with concentrations ranging from 157 to 340  $\mu\text{mol/L}$ . The concentration of  $\text{Na}^+$  and  $\text{K}^+$  ranges from 83 to 194  $\mu\text{mol/L}$  and from 24.7 to 54.4  $\mu\text{mol/L}$ , respectively. With regard to the trace elements, Sr concentrations range from 0.75 to 2.07  $\mu\text{mol/L}$ , while Rb concentrations are very low, ranging from 0.0015 to 0.0030  $\mu\text{mol/L}$ .  $\text{SO}_4^{2-}$  concentrations range from 139 to 381  $\mu\text{mol/L}$ ,

while the concentrations of  $\text{Cl}^-$  and  $\text{NO}_3^-$  range from 68 to 160  $\mu\text{mol/L}$  and from 76 to 136  $\mu\text{mol/L}$ , respectively.

The  $\delta^{88}\text{Sr}$  values of the river water vary from 0.147‰ to 0.661‰, and the  $^{87}\text{Sr}/^{86}\text{Sr}^*$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  values vary from 0.708576 to 0.710542, and from 0.708487 to 0.710336, respectively. The  $^{87}\text{Sr}/^{86}\text{Sr}^*$  is generally slightly larger than  $^{87}\text{Sr}/^{86}\text{Sr}$  by 0.000044 to 0.000222. A robust linear correlation is found between  $^{87}\text{Sr}/^{86}\text{Sr}^*$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  values with a correlation coefficient of 0.996 ( $N = 18$ ,  $p < 0.0000001$ ) (Fig. 2a), with the difference between them, defined as  $\Delta^{87}\text{Sr}/^{86}\text{Sr} = ^{87}\text{Sr}/^{86}\text{Sr}^* - ^{87}\text{Sr}/^{86}\text{Sr}$ , linearly correlating to  $\delta^{88}\text{Sr}$  (Fig. 2b). Thus, the observed variation in both the  $^{87}\text{Sr}/^{86}\text{Sr}^*$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  values throughout the year-long study are identical. To compare with previous results, which are all traditional  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements, only the  $^{87}\text{Sr}/^{86}\text{Sr}$  variation is considered in the following discussion.

The temporal variations in the Sr isotope ( $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ), Rb/Sr, and  $\delta^{13}\text{C}_{\text{DIC}}$  data are shown in Fig. 3. The water temperature, river flux, and pH are also displayed together for comparison. The  $\delta^{13}\text{C}_{\text{DIC}}$  values vary from  $-6.6\text{‰}$  to  $-13.0\text{‰}$ , with the most negative value occurring during the flood period of June 2010, which is also accompanied by the lowest pH values. The variation in  $\delta^{88}\text{Sr}$  values is very similar to that for  $^{87}\text{Sr}/^{86}\text{Sr}$ , with high values generally occurring during periods of large river flux (Fig. 3). The positive correlation between  $\delta^{88}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  is significant, with a correlation coefficient of 0.73 ( $N = 19$ ,  $p < 0.0003$ ).

#### 5. Discussion

##### 5.1. Seasonal changes in radiogenic Sr isotope values of the river water and implications for silicate weathering

The weathering of carbonates is generally the dominant contributor of major ions to the waters of the Xijiang River; however, the contribution from the weathering of silicate rocks can also be identified in some areas (Xu and Liu, 2007). This observation is consistent with the predominance of carbonate rocks within the Xijiang River drainage basin. Fig. 4a shows the  $\text{Ca}^{2+} - \text{Mg}^{2+} - \text{Na}^+ + \text{K}^+$  discrimination diagram of water from the main stream at Nanpanjiang and Beipanjiang, the upper reaches of the Xijiang River (Xu and Liu, 2007), and the time-series samples from the Wuzhou (Gao et al., 2009) and Guiping (this study) stations. The water samples from

**Table 1**  
The Sr isotopes, DIC  $\delta^{13}\text{C}$  and selected anions, major and trace elements of the river water.

Sample ID <sup>a</sup>	Decimal year	T (°C)	pH <sup>b</sup>	TDS (mg/L)	Flux <sup>c</sup> ( $\text{m}^3/\text{s}$ )	Na ( $\mu\text{mol/L}$ )	Mg ( $\mu\text{mol/L}$ )	K ( $\mu\text{mol/L}$ )	Ca ( $\mu\text{mol/L}$ )	Rb ( $\mu\text{mol/L}$ )	Sr ( $\mu\text{mol/L}$ )	$\text{Cl}^-$ ( $\mu\text{mol/L}$ )	$\text{NO}_3^-$ ( $\mu\text{mol/L}$ )	$\text{SO}_4^{2-}$ ( $\mu\text{mol/L}$ )	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{88}\text{Sr}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$^{87}\text{Sr}/^{86}\text{Sr}$
GP2009-7-31	2009.58	26.5	7.965	87	2180	82	168	33.6	900	0.0215	0.89	68	76	139	-9.82	0.240 ± 0.010	0.709611 ± 9	0.709520 ± 5
GP2009-8-14	2009.62	27.8	8.266	117	751	118	256	33.4	1230	0.0186	1.53	79	104	230	-7.75	0.147 ± 0.010	0.708762 ± 9	0.708719 ± 4
GP2009-9-12	2009.70	28.1	8.154	121	216	143	298	34.9	1306	0.0191	1.94	92	114	299	-6.66	0.195 ± 0.010	0.708576 ± 8	0.708487 ± 4
GP2009-9-26	2009.74	28.6	8.195	100	246	146	253	33.8	1070	0.0219	1.46	103	98	230	-8.34	0.186 ± 0.008	0.709000 ± 10	0.708926 ± 6
GP2009-10-8	2009.77	29.2	8.754	130	268	147	269	37.2	1025	0.0217	1.58	101	88	255	-9.37	0.210 ± 0.010	0.708829 ± 9	0.708751 ± 5
GP2009-11-5	2009.85	24.4	8.556	136	205	165	287	40.7	1220	0.0241	1.78	121	118	282	-6.90	0.223 ± 0.010	0.708733 ± 9	0.708648 ± 5
GP2009-12-3	2009.92	20.9	8.623	147	192	185	315	45.1	1315	0.0233	2.07	119	116	301	-6.64	0.181 ± 0.008	0.708630 ± 9	0.708565 ± 4
GP2010-1-2	2010.01	17.4	8.432	153	150	179	324	41.9	1276	0.0210	2.07	109	117	325	-6.59	0.196 ± 0.010	0.708670 ± 9	0.708595 ± 5
GP2010-1-29	2010.08	15.9	8.037	133	500	194	252	54.4	996	0.0297	1.40	160	114	280	-8.44	0.212 ± 0.010	0.709373 ± 10	0.709314 ± 6
GP2010-2-12	2010.12	16.1	8.065	150	-	165	286	41.7	1273	0.0215	1.57	115	110	259	-6.79	0.310 ± 0.011	0.708980 ± 12	0.708888 ± 7
GP2010-2-26	2010.16	18.6	8.387	163	160	174	322	48.4	1298	0.0241	1.86	124	110	284	-7.31	0.337 ± 0.010	0.708880 ± 10	0.708763 ± 5
GP2010-3-27	2010.24	17.8	8.106	151	150	187	340	49.5	1297	0.0228	2.05	126	119	381	-9.00	0.254 ± 0.012	0.708798 ± 10	0.708713 ± 6
GP2010-4-24	2010.31	19.7	7.954	104	1120	172	213	38.8	799	0.0251	0.99	131	133	256	-8.54	0.661 ± 0.011	0.710542 ± 12	0.710336 ± 7
GP2010-5-29	2010.41	25.1	8.213	126	3400	147	246	35.8	1029	0.0221	1.34	131	118	258	-9.54	0.418 ± 0.011	0.709459 ± 10	0.709325 ± 6
GP2010-6-19	2010.47	23.3	7.808	95	14700	83	157	29.4	816	0.0190	0.75	91	110	165	-13.0	0.342 ± 0.011	0.710383 ± 10	0.710291 ± 5
GP2010-7-3	2010.50	24.8	7.852	113	4630	93	182	25.3	951	0.0178	0.95	70	136	164	-9.35	0.585 ± 0.010	0.709760 ± 9	0.709538 ± 5
GP2010-7-17	2010.54	27.0	8.142	124	960	106	214	24.7	1138	0.0152	1.23	72	106	235	-9.12	0.357 ± 0.010	0.709229 ± 9	0.709099 ± 4
GP2010-7-31	2010.58	26.0	8.028	132	2450	102	228	28.9	1255	0.0174	1.25	78	114	278	-9.71	0.482 ± 0.011	0.709225 ± 9	0.709048 ± 5
GP2010-8-14	2010.62	27.1	8.078	129	820	94	209	26.5	1170	0.0158	1.28	67	115	260	-9.48	0.294 ± 0.010	0.709108 ± 9	0.708991 ± 5

<sup>a</sup> "-" indicates that the data has not recorded in time, and the data was not available after the update of the website.

<sup>b</sup> The numbers in the sample ID indicate the date of sampling. For example GP2009-7-31 indicates that the sample was collected on July 31, 2009.

<sup>c</sup> The errors for the pH are generally from 0.002 to 0.003.

<sup>d</sup> The flux was recorded from the web of the instant hydrological information for the main rivers in China (<http://xxfb.hydroinfo.gov.cn>).

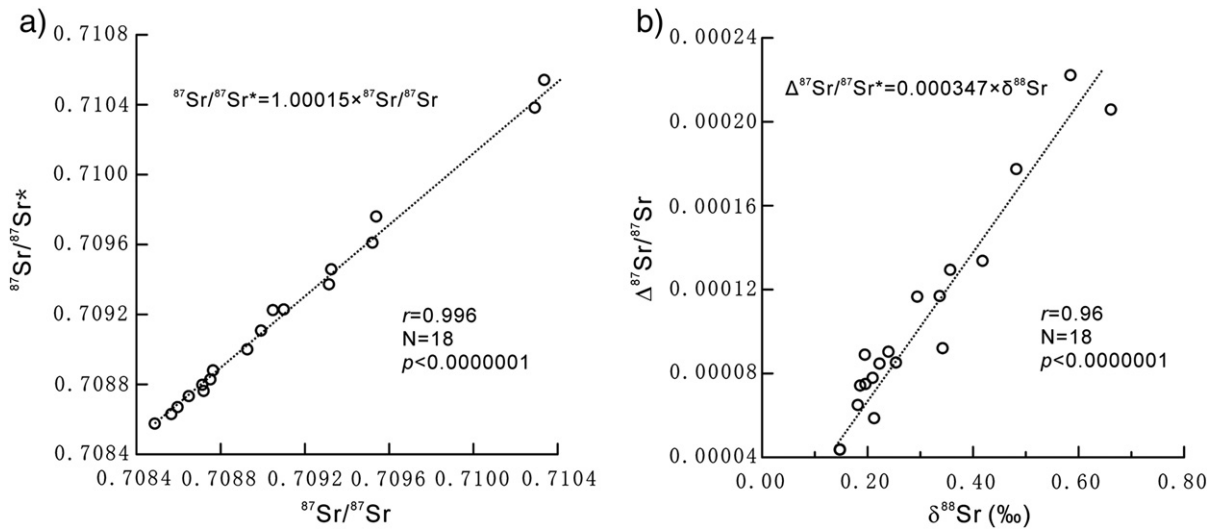


Fig. 2. Correlations between a)  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}^*$ , and b)  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88}\text{Sr}$ .

Wuzhou and Guiping, as well as those from Beipanjiang, are all dominated by  $\text{Ca}^{2+}$ , which accounts for over 75% of the cations (Fig. 4a). This result supports the notion that weathering of carbonate rocks is the dominant source of major ions to the Xijiang River throughout the year (Xu and Liu, 2007), including at the Guiping station examined in this study.

Weathering of silicate rocks, however, also contributes to the chemistry of the Xijiang River at Nanpanjiang (Xu and Liu, 2007), as these samples plot slightly away from the time-series samples at Guiping and Wuzhou (Fig. 4a). This contribution from silicate rocks can be seen more clearly in the  $^{87}\text{Sr}/^{86}\text{Sr}-\text{Ca}^{2+}/\text{Mg}^{2+}$  diagram (Fig. 4b), as the products of weathering from silicate rocks generally have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Krishnaswami et al., 1992) and lower  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratios (Gaillardet et al., 1999). The samples from Nanpanjiang are clearly influenced by the weathering of silicate rocks, while those from Beipanjiang are predominantly influenced by the weathering of carbonate rocks (Xu and Liu, 2007). The time-series samples at Guiping lie between those from Beipanjiang and Nanpanjiang, with the majority plotting close to the zone of dominant carbonate weathering. However, some of the samples from Guiping are located in the Nanpanjiang zone (Fig. 4b), indicating a likely contribution from the weathering of silicate rocks to river waters at Guiping during some seasons.

Changing  $^{87}\text{Sr}/^{86}\text{Sr}$  values in river water can be used to estimate the dominant source of the weathered material, as high  $^{87}\text{Sr}/^{86}\text{Sr}$  values are thought to be indicative of a greater contribution from the weathering of silicate rocks (Krishnaswami et al., 1992). Rb/Sr ratios in river water can also be used to discriminate between silicate and carbonate weathering, as Rb is primarily sourced from the weathering of silicate rocks, while Sr is mainly sourced from the weathering of carbonate rocks. Thus, enhanced weathering of silicate rocks in the drainage basin may result in higher Rb/Sr values in river water. At Guiping,  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr values covary with a robust correlation coefficient of 0.91 ( $N=19$ ,  $p<0.0000001$ ) (Fig. 5a). The covariance of these two records suggests they can be considered a reliable proxy for the variable influence of silicate rock weathering in the drainage basin. As shown in Fig. 3, an enhanced contribution from the weathering of silicate rocks, as indicated by higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios, generally occurs during periods of large river flux. A power function relationship exists between the  $^{87}\text{Sr}/^{86}\text{Sr}$  values and the magnitude of river flux (Fig. 5b). If all the data are included, a robust correlation coefficient of 0.79 ( $N=19$ ,  $p<0.00003$ ) is obtained; however, the correlation markedly improves to 0.91 ( $N=18$ ,  $p<0.0000001$ ) if the data collected on 24 April 2010 are excluded. The sample collected on this day differed somewhat from other samples, as it yields the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.710336) and Rb/Sr (0.0252) ratios, the

lowest  $\text{Ca}^{2+}$  concentration (799  $\mu\text{mol/L}$ ), and almost the highest  $\text{Cl}^-$  (131  $\mu\text{mol/L}$ ) and  $\text{NO}_3^-$  (133  $\mu\text{mol/L}$ ) concentrations of any of the samples collected at Guiping (Table 1). The river flux during that day, however, was moderate (1120  $\text{m}^3/\text{s}$ ). It may be that there was some contribution from a specific and unusual source during that period; however, this source cannot be identified using the existing data alone. Despite this exception, the correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  and river flux is significant. The seasonal change in the contribution of water from groundwater sources may account for the correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  and river flux. During the dry season, groundwater, with generally low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios influenced by the regional carbonate geology, is a dominant source of water to the Xijiang River (Han and Liu, 2004; Gao et al., 2009). In contrast, during the rainy season there is a large contribution of surficial water to the riverwater flux. Giving that surficial water has high concentrations of Sr, with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from soils developed from silicate rocks, the contribution from the weathering of silicate rocks to the waters of the Xijiang River is enhanced during the rainy season.

Such seasonal trends in the contribution from weathering of silicate rocks are converse to those observed in the rivers of the Himalayan region, where the contribution of silicate rock weathering to river water is smaller during monsoonal seasons than that during other seasons (Rai and Singh, 2007; Tripathy et al., 2010). Different controls on the weathering of silicate rocks in these two regions may account for such discrepancies. In high mountain regions such as the Himalaya, physical weathering is very active while chemical weathering is much less intense. During the monsoon season, the area affected by weathering enlarges, but the period of water–rock interaction is reduced (Rai and Singh, 2007; Tripathy et al., 2010). Because weathering rates for carbonate rocks are much higher than that for silicate rocks, the weathering of carbonate rocks is significantly enhanced during the monsoon season, with a relatively small corresponding increase in silicate rock weathering. As a result, the contribution from the weathering of silicate rocks to the river water chemistry decreases during the monsoon season (Rai and Singh, 2007; Tripathy et al., 2010). In contrast, intense chemical weathering occurs in the tropical region of South China, where the Xijiang River drainage basin is located, as evidenced by the numerous laterites and lush vegetation in this region. The decomposition of plants in the warm and humid environment not only decreases the pH of soils and saprolites, to ~5–6 pH units (Ma et al., 2007), but also provides large quantities of dissolved organic material that can significantly improve the mobility of conservative elements, and which favors intensive chemical weathering of silicate rocks (Oliva et al., 1999; Ma et al., 2007). During rainy seasons with large river fluxes, vast quantities of the weathering products of

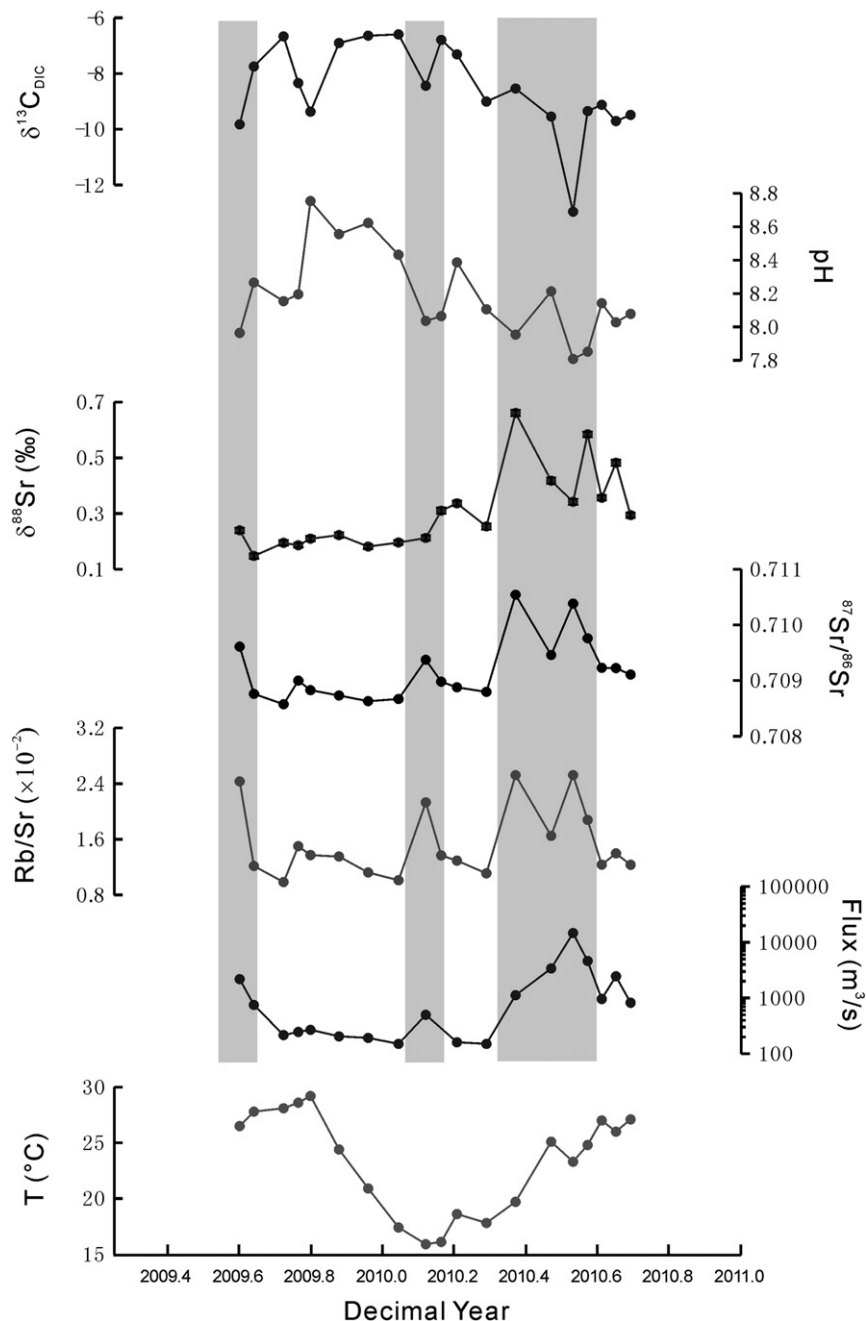


Fig. 3. Temporal variations in water temperature, river flux, pH,  $\delta^{13}\text{C}_{\text{DIC}}$ , Rb/Sr,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\delta^{88}\text{Sr}$  of the river water at Guiping. The shaded bars mark periods of increased Rb/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$ .

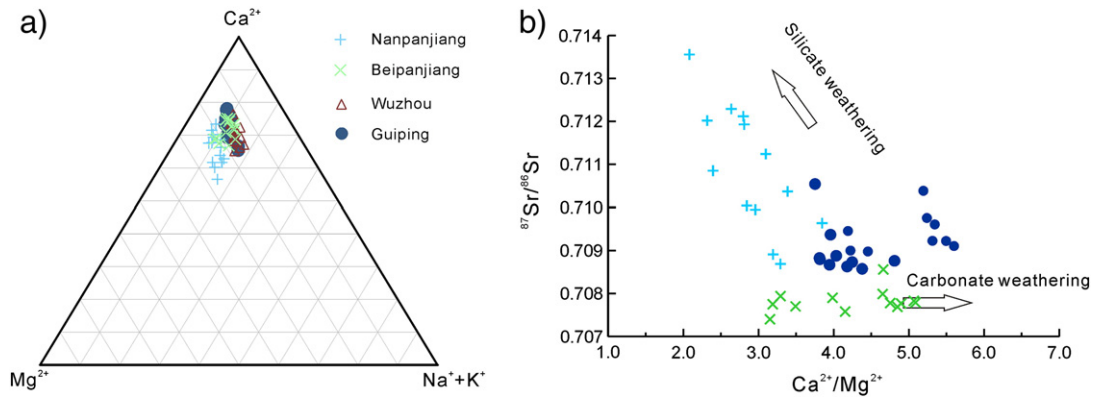
silicate rocks, contained in laterite soils and saprolites, are transported to rivers. As a result, the contribution to river water from the weathering of silicate rocks increases, leading to higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios, as observed in the river water at Guiping.

The correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$ , and pH and  $\delta^{13}\text{C}_{\text{DIC}}$  in the river water lends further weight to this assertion (Fig. 5c and d). The  $^{87}\text{Sr}/^{86}\text{Sr}$  values show a significant negative correlation with pH values, with a correlation coefficient of  $-0.70$  ( $N=19$ ,  $p<0.0005$ ). This agrees with the fact that lower pH favors the chemical weathering of silicate rocks (Ma et al., 2007). Additionally, a significant negative correlation is seen between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  in these waters (Fig. 5d). If all the data are included, a correlation coefficient of  $-0.69$  ( $N=19$ ,  $p<0.0006$ ) is obtained, with a significantly improved correlation of  $-0.86$  ( $N=18$ ,  $p<0.000003$ ) if the outlying data from 24 April 2009 are excluded. More negative  $\delta^{13}\text{C}_{\text{DIC}}$  values indicate a larger contribution from soils derived from the weathering of silicate rocks, as

these contain organic materials with relatively negative  $\delta^{13}\text{C}$  values (Li et al., 2008). It is therefore suggested that the high  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios observed during periods of large river flux in the Xijiang River, are indicative of an enhanced contribution from the weathering of silicate rocks during the rainy season.

### 5.2. Seasonal changes in stable Sr isotope values

As shown in Fig. 3, the seasonal variation in  $\delta^{88}\text{Sr}$  values at Guiping is similar to that observed in  $^{87}\text{Sr}/^{86}\text{Sr}$  values, as evidenced by the significant correlation between them (Fig. 6). The low  $\delta^{88}\text{Sr}$  ( $<0.3\%$ ) and low  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $<0.7092$ ) values highlighted in the shaded region in Fig. 6 are well within the range of marine carbonates (Halicz et al., 2008; Ohno et al., 2008; Krabbenhoft et al., 2010), indicating that the Sr in these water samples was largely sourced from the dissolution of carbonate rocks. This observation agrees with the



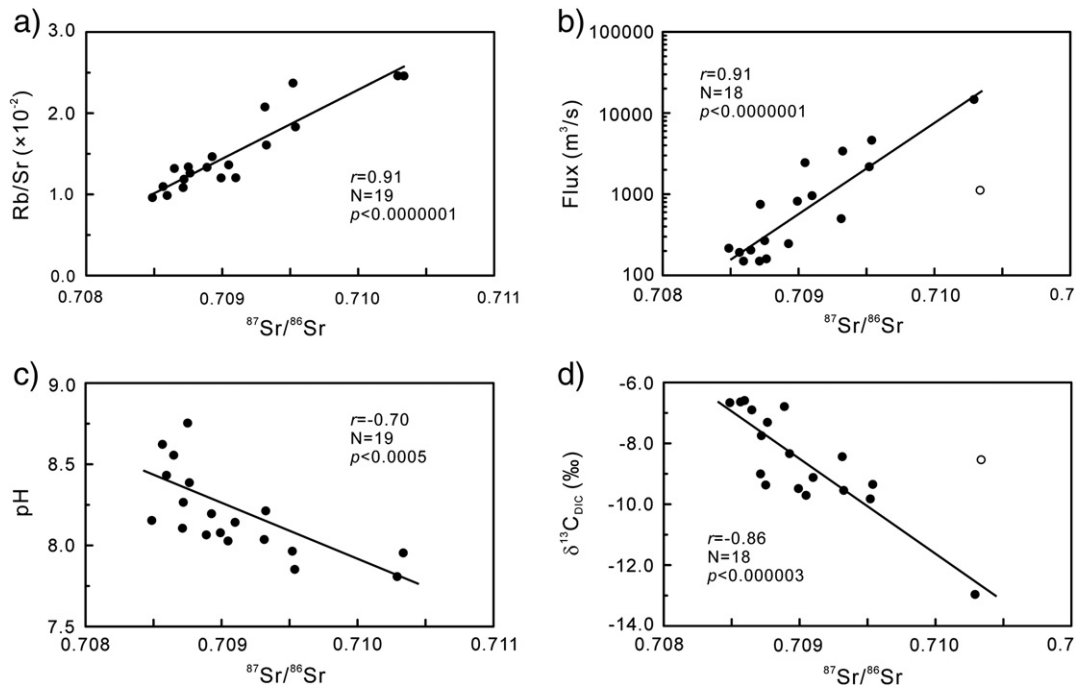
**Fig. 4.** a)  $\text{Ca}^{2+} - \text{Mg}^{2+} - \text{Na}^+ + \text{K}^+$ , and b)  $\text{Ca}^{2+}/\text{Mg}^{2+} - ^{87}\text{Sr}/^{86}\text{Sr}$  diagrams showing the sources of the major ions and Sr in the Xijiang River. The arrows indicate the trends for weathering of carbonate and silicate rocks, respectively.

The Nanpanjiang and Beipanjiang data are from Xu and Liu (2007), while data from Wuzhou are from Gao et al. (2009).

conclusion stated above that weathering of carbonate contributes to the main of the chemistry of the river water. Consequently, the river water samples out of this shaded region in Fig. 6, may be influenced by the weathering of silicate rocks.

Several samples from Guiping have large  $\delta^{88}\text{Sr}$  values ( $>0.4\%$ ) that are out of the range of terrestrial rocks (generally  $0.2\%$ – $0.3\%$ ; Moynier et al., 2010; Charlier et al., 2012). According to de Souza et al. (2010), incipient chemical weathering of silicate rocks may not cause significant Sr isotopic fractionation, meaning the  $\delta^{88}\text{Sr}$  of the released Sr is similar to that of the parent rocks. This appears to not be the case for the Xijiang River, when considering the significantly larger  $\delta^{88}\text{Sr}$  values relative to those of terrestrial rocks. One explanation may be that the study by de Souza et al. (2010) was carried out in temperate regions, where the intensity of chemical weathering is relatively low, whereas chemical weathering in the tropical region of the Xijiang River drainage basin is intensive. Additionally, it has been

shown that the isotopes of conservative elements, such as Nd and Hf, as well as Sr isotopes, can be altered significantly during extreme weathering of silicate rocks (Ma et al., 2010). Fractionation of stable Sr isotopes has also been indicated by Halicz et al. (2008), who demonstrated that the products of silicate rock weathering, such as those from terra-rossa soils, generally show negative  $\delta^{88}\text{Sr}$  values ( $\sim -0.17\%$ ). This value is significantly lower than those reported for terrestrial silicate rocks (Halicz et al., 2008). Supposing a mass balance for Sr stable isotopes during chemical weathering, the negative  $\delta^{88}\text{Sr}$  values observed in the weathering products indicates the released Sr may have higher  $\delta^{88}\text{Sr}$  values than those of the parent rocks. This agrees well with the high  $\delta^{88}\text{Sr}$  values observed in the waters of the Xijiang River, as the Sr in river water is composed of Sr released during chemical weathering. It is therefore clear that the high  $\delta^{88}\text{Sr}$  values, in addition to the high  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios, in the Xijiang River water may be derived from intensive



**Fig. 5.** Correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  and a) the Rb/Sr ratio, b) flux, c) pH, and d)  $\delta^{13}\text{C}_{\text{DIC}}$  of the river water. The open circle in b) and d) marks the sample collected on 24 April 2009, and it is not included in the calculation for the regression shown in the corresponding diagram.

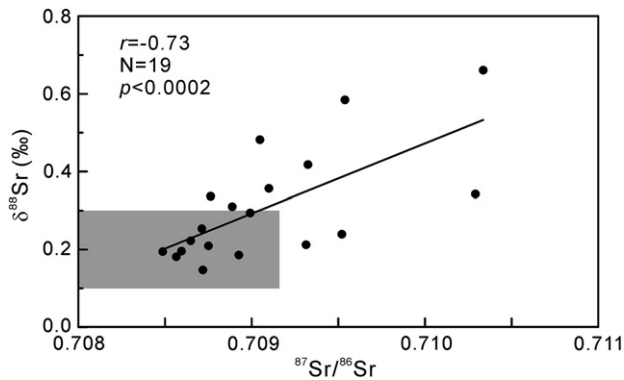


Fig. 6. Correlation between the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88}\text{Sr}$  values of sampled river water. The shaded area shows the range in values of marine carbonates.

weathering of silicate rocks. However, stable Sr isotope fractionation during intensive chemical weathering requires further investigation, in particular the study of the weathering profiles of silicate rocks to determine the exact mechanism behind the fractionation process.

### 5.3. Sr isotopic budgets for the Xijiang River

Giving that the isotopic composition of dissolved Sr in large rivers may influence Sr isotope values in the global oceans (Palmer and Edmond, 1989), more precise Sr isotopic budgets of rivers can provide a better estimate of marine Sr isotope variation. As the seasonal variability in Sr concentrations and isotopic composition can be large, using the flux-weighted averages from a year-long time-series would be more precise than using data from only the rainy or dry seasons. Current available values for the Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  for the Xijiang River are  $1.27 \mu\text{mol/L}$  and  $0.71068$ , respectively (Gaillardet et al., 1999). This Sr concentration value is close to the median value of those observed at Guiping, but this  $^{87}\text{Sr}/^{86}\text{Sr}$  value is similar to the  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the Xijiang River during periods of large river flux. In this study, the flux-weighted averages of Sr concentration,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\delta^{88}\text{Sr}$  for the water at Guiping can be calculated from the year-long time-series data, yielding values of  $1.00 \mu\text{mol/L}$ ,  $0.70972$ ,  $0.70960$ , and  $0.38\%$ , respectively. The flux-weighted average Sr concentration is slightly lower than the previous result by Gaillardet et al. (1999). With respect to the radiogenic Sr isotopes, the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of Gaillardet et al. (1999) was calibrated by  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ ; thus, only the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Xijiang River water could be compared with the previous results. The flux-weighted average  $^{87}\text{Sr}/^{86}\text{Sr}$  value at Guiping is  $\sim 0.001$  lower than that reported by Gaillardet et al. (1999). These discrepancies in Sr concentration and isotopic composition may arise because an instantaneous observation (Gaillardet et al., 1999) is compared with the average of a time-series observation (this study) (Tripathy et al., 2010). However, considering the large seasonal variations in Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the Xijiang River water, such discrepancies are small. It is therefore clear that our flux-weighted averages can be used as estimates for the Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  budgets of the Xijiang River.

The flux-weighted average  $\delta^{88}\text{Sr}$  for the Xijiang River,  $0.38\%$ , is similar to that for the Changjiang River reported by Krabbenhoft et al. (2010). This value is among the highest reported for large rivers worldwide (Krabbenhoft et al., 2010), and is close to that of seawater. As discussed above, the high  $\delta^{88}\text{Sr}$  values in river water appear to be sourced from the intensive weathering of silicate rocks. Rivers with large areas of drainage located in tropical/sub-tropical regions, like the Xijiang and Changjiang rivers, are likely to be important contributors to the high  $\delta^{88}\text{Sr}$  value of the global ocean. It is therefore clear that large rivers draining through tropical/sub-tropical regions could play an important role in regulating the stable Sr isotope budget of the global ocean.

## 6. Summary

We reported a year-long time-series of the radiogenic and stable Sr isotope composition of the Xijiang River. Coupled with other chemical records of the river water, such as the concentrations of the major anions, and major and trace elements, the seasonal variation in Sr isotopic composition is linked to seasonal changes in chemical weathering across the drainage basin. The main findings of this study are as follows.

- 1) The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the river water ranges from  $0.708487$  to  $0.710336$ , with high values generally occurring during periods of large river flux. The  $^{87}\text{Sr}/^{86}\text{Sr}$  values, as well as the composition of the major ions, indicates that weathering of carbonate rocks is the dominant source of major ions and Sr in the Xijiang River throughout the year. However, the contribution from weathering of silicate rocks is enhanced during periods of large river flux, as inferred from increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios during these periods. This increase is generally accompanied by decreasing pH and  $\delta^{13}\text{C}_{\text{DIC}}$  values, indicating that an increased contribution from the weathering of silicate rocks may be caused by increased weathering of soils and saprolites during the rainy season, as these materials have been subjected to intensive chemical weathering in the drainage basin of the Xijiang River.
- 2) The  $\delta^{88}\text{Sr}$  values of the river water show large seasonal variations, ranging from  $0.147\%$  to  $0.661\%$ , with high  $\delta^{88}\text{Sr}$  generally corresponding to high  $^{87}\text{Sr}/^{86}\text{Sr}$ . During periods of low river flux, the  $\delta^{88}\text{Sr}$  values are well within the range of marine carbonate rocks, suggesting the Sr is predominantly sourced from the weathering of carbonate rocks. The  $\delta^{88}\text{Sr}$  values during periods of large river flux are even higher than those reported from terrestrial rocks, and are likely sourced from intensive weathering of silicate rocks.
- 3) Considering the large seasonal changes in Sr concentration and isotopic composition in the river water, the flux-weighted averages of these parameters were calculated to estimate their budgets for the Xijiang River. This yielded values of  $1.00 \mu\text{mol/L}$ ,  $0.70972$ ,  $0.70960$ , and  $0.38\%$  for Sr concentration,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\delta^{88}\text{Sr}$ , respectively. The Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  values are close to previous estimates by Gaillardet et al. (1999). The  $\delta^{88}\text{Sr}$  value is similar to that observed in the Changjiang River, which is amongst the highest values reported from the large rivers of the world, and close to that of seawater. We therefore propose that large rivers draining through tropical/sub-tropical regions could play an important role in modulating the stable Sr isotopic budget of the global ocean.

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