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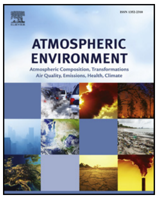

Ca and Sr isotope compositions of rainwater from Guiyang city, Southwest China: Implication for the sources of atmospheric aerosols and their seasonal variations

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ABSTRACT

Rainwater samples collected from Guiyang city in southwestern China between May 2009 and December 2010 were analyzed to measure their calcium and strontium isotope compositions. The results show that Ca^{2+} is the most abundant cation in these rainwater samples, while SO_4^{2-} is the most abundant anion. Most rainwater samples are alkaline, with a volume-weighted mean (VWM) pH value of ~6.2 (a 1.2-unit increase since 2008). This can be explained by the neutralization of rainwater acidity by the dissolution of atmospheric aerosols in the form of calcium-rich soil and other anthropogenic dust, which are increasing because of rapid urbanization. Both stable ($\delta^{44/40}$Ca and $\delta^{88/86}$Sr) and radiogenic (^{87}Sr/^{86}Sr) isotope compositions of rainwater show variations correlating with each other and with the inverse of Sr or Ca concentrations. They also correlated with the concentration ratio of $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$ —an index reflecting the anthropogenic input relative to soil dust. Based on our results, three major reservoirs can be inferred to have contributed to rainwater chemistry in Guiyang city: (1) a carbonate aerosol source characterized by low ^{87}Sr/^{86}Sr ($\leq$~0.708), $\delta^{88/86}$Sr ($\leq$~0.32‰) and $\delta^{44/40}$Ca (~0.5‰), very low $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$, and low $1/Ca^{2+}$ and $1/Sr^{2+}$; (2) a silicate aerosol source characterized by relatively high ^{87}Sr/^{86}Sr ($\geq$0.717), $\delta^{88/86}$Sr ($\geq$~0.34‰) and $\delta^{44/40}$Ca (~0.8‰), very low $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$, low $1/Ca^{2+}$ and $1/Sr^{2+}$; and (3) an anthropogenic component containing low ^{87}Sr/^{86}Sr (~0.708), $\delta^{88/86}$Sr (~0.30‰) and high $\delta^{44/40}$Ca (~0.8‰), and high $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$. The chemistry of solutes in Guiyang rainwater can be explained by (1) dissolution of carbonate and silicate aerosols, as well as the anthropogenic inputs including seasonal farming activities; (2) tightened environmental protection regulations; (3) higher precipitation volumes in 2010; and possibly (4) the increased combustion of coal for heating and electricity in winter. This study demonstrated that a combination of elemental compositions, stable Ca and Sr, and radiogenic Sr isotope compositions in rainwater can be used to trace the sources of atmospheric aerosols.

1. Introduction

Atmospheric aerosols play important roles in Earth's energy budget. They act as nucleation centers, which facilitate the condensation of water droplets and ice crystals (Haywood and Boucher, 2000). Once they are dissolved in water droplets, the physical and chemical properties of these aerosols can be altered (Lohmann and Feichter, 2005). Rainwater chemistry, therefore, reflects the interaction among various types of aerosols and minor atmospheric gases averaged over a large region; as a result, it can be used to trace aerosol sources (Roy and Negrel, 2001; Chetelat et al., 2005; Negrel et al., 2007).

A growing number of investigations are focusing on precipitation chemistry in big cities of China. They have concluded that rainwater is mostly acidic due to abundant sulfate and nitrate aerosols originating from human activities related to rapid economic growth and increasing fossil fuel consumption (Aas et al., 2007; Huang et al., 2008; Zhao et al., 2008; Xu and Han, 2009; Han et al., 2010; Wu et al., 2012; Wu and Han, 2015; Rao et al., 2015). A recent survey by the Ministry of

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Environmental Protection Administration of China (MEP) showed that about 27% of Chinese cities are affected by acid precipitation (Ministry of Ecology and Environment of the People's Republic of China, 2017). However, previous studies have also suggested that acid precipitation across southwestern China was significantly neutralized by alkaline dust: a process manifested by the increase of rainwater pH values across the region related to the release of alkaline earth metal ions (e.g., Ca^{2+}, Mg^{2+}, Sr^{2+}, Han and Liu, 2006; Han et al., 2011).

Elemental concentrations and pH values could provide abundant information about the chemical properties of the dissolved constituents of rainwater. However, the isotopic compositions of metal ions (e.g., Ca^{2+}, Mg^{2+}, Sr^{2+}) are more effective tools for fingerprinting the source of aerosols because metal concentrations and pH values are controlled not only by the chemical signatures and concentrations of aerosols in the atmosphere; but also by the solubility of aerosols in rainwater and the concentration of minor atmospheric gases (e.g., CO_2 and SO_2). For example, radiogenic Sr isotope composition ($^{87}Sr/^{86}Sr$) has often been used to indirectly trace the sources of Ca ions. These ions are an essential component in rainwater. Unfortunately, it can be hard to distinguish among various sources solely based on the concentration due to the similar geochemical properties of Sr and Ca (Aberg et al., 1989; Nakano and Tanaka, 1997; Probst et al., 2000; Chatterjee and Singh, 2012) and the ease of measuring $^{87}Sr/^{86}Sr$ ratios (Krabbenhoft et al., 2009; Neymark et al., 2014).

Recent analytical advances allow us to precisely determine stable $\delta^{88/86}Sr$ and $\delta^{44/40}Ca$ values in rainwater (Schmitt and Stille, 2005; Fantle and Tipper, 2014; Pearce et al., 2015a,b), greatly expanding our capability to trace potential sources of aerosols and determine transportation processes. For example, Schmitt and Stille (2005) noticed that the Ca isotope compositions of rainwater were associated with a local carbonate source, while Fantle et al. (2012) concluded that the $\delta^{44/40}Ca$ values of rainwater are mainly controlled by calcite dust derived in semi-arid systems. Because of the limited number of published rainwater Ca isotope compositions, the magnitude and mechanism of the isotopic fractionation during atmospheric processes remain elusive (e.g., Fantle and Tipper, 2014). Moreover, radiogenic $^{87}Sr/^{86}Sr$, the product of the radioactive decay of ^{87}Rb to ^{87}Sr, has frequently been used to trace the source of ions in rainwater (e.g., Herut et al., 1993; Nakano and Tanaka, 1997). It has long been taken for granted that compositions of stable Sr isotopes (e.g., $\delta^{88/86}Sr$) exhibit negligible variations during chemical weathering because of the small relative mass differences between ^{88}Sr and ^{86}Sr. However, recent studies have shown that Sr does experience mass fractionation during terrestrial exogenic cycling (Stevenson et al., 2016). In particular, lighter Sr isotopes are preferentially incorporated into biogenic and inorganic Ca-carbonates, whereas seawater concentrates heavy Sr isotopes (Fietzke and Eisenhauer, 2006), as is the case for Ca isotopes (Skulan et al., 1997). Pearce et al. (2015a, b) concluded that $\delta^{88/86}Sr$ values of rainwater from Paris reflected the extent of mixing between marine, terrestrial and anthropogenic aerosols.

This study aims to present and characterize the isotopic compositions of Ca ($\delta^{44/40}Ca$), radiogenic Sr ($^{87}Sr/^{86}Sr$), and stable Sr ($\delta^{88/86}Sr$) for rainwater collected from Guiyang city, southwestern China. We discuss the application of Ca and Sr isotopes combined with other chemical attributes of rainwater, to effort to determine the origin of water-soluble ions in rainwater, for water samples collected between May 2009 and December 2010. Our results might be representative of acid precipitation in other cities of developing countries that suffered from serious pollution and contamination.

2. Sampling site

Samples for this study were collected within the city of Guiyang (N 26.34°, E 106.43°), southwestern China (Fig. 1). This city, one of the most polluted in China, has large, dense population, as well as a rapidly increasing level of traffic. The city of Guiyang has been seriously affected by acid precipitation since 1970 (Zhao et al., 1988; Han and Liu, 2006; Han et al., 2011; Wu et al., 2012). According to the Guiyang Economic and Social Development Statistics Bulletin (2011), the population of Guiyang city exceeded 3.5 million by the end of 2011, while the industrial output increased from 7.7 billion Chinese yuan in 1989 to 138.3 billion Chinese yuan in 2011. The number of cars in the city of Guiyang exceeded 645,000 by the end of year 2011.

Surrounded by mountains, the Guiyang city sits in a wide karst valley at an elevation of about 1000 m. The lithology in this region is dominated by sedimentary strata, the bulk of which are comprised of carbonate and clastic rocks (Han et al., 2011). Guiyang has a sub-tropical climate, and the diurnal average temperature ranges from −1 °C in winter to 30 °C in summer. The dry season lasts from November to April, while the wet season lasts from May to October. The annual average precipitation in the city of Guiyang ranges from 900 to 1500 mm, 80% of which occurs between May and August.

3. Sampling and analytical methods

3.1. Sampling and chemical analysis

The polypropylene sampler used for this study was positioned about 15 m above the ground level on the roof of the office building at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The sampling processes followed those described previously (Han et al., 2011). Rainwater samples were collected manually using a funnel sampler located about 120 cm above the roof. This sampler was cleaned with HCl acid (2–3 N), soaked in Milli-Q water (18.2 MΩ cm) for 48 h, and then rinsed in Milli-Q water again and dried down completely in a clean laboratory (class 1000) before each use. To prevent contamination from dry deposition, the sampler was covered with a plastic lid, which was removed just before the onset of a rainfall. A total of 47 rainwater samples were collected between May 2009 and December 2010, mostly during the rainy season. A few samples were collected after September during the dry season. One rainwater sample from each month was chosen for measuring isotopic compositions. In total, the isotopic compositions of 13 different rainwater samples were obtained.

At the end of rain events, pH values were measured immediately on site using a pH meter (Mettler Toledo, German); all rainwater samples were filtered through 0.22 μm Millipore membrane filters using a pre-cleaned Nalgene apparatus. The filtrate was then divided into two aliquots, one of which was stored in a polyethylene bottle for the measurement of anion concentrations. The other was acidified with ultra-pure nitric acid to a pH of < 2 and stored in a polyethylene bottle for the measurement of cation concentrations, and Ca and Sr isotope ratios. The polyethylene bottle was pre-cleaned according to the following procedure: (1) the bottles were washed by detergent and then rinsed in Milli-Q water; (2) the bottles were soaked in HNO_3 (6–8 N) and HCl (~6 N) for 48 h each, and rinsed with Milli-Q water; (3) the bottles were soaked in HCl (2–3 N) diluted from distillated HCl for more than 48 h and in Milli-Q water for 48 h, before being rinsed with Milli-Q water in the clean laboratory.

The concentrations of major anions (including F^-, Cl^-, NO_3^-, and SO_4^{2-}) were measured *via* ion chromatography using a Dionex DX-120 system, the detection limits of F^-, Cl^-, NO_3^-, and SO_4^{2-} ions were found to be 0.03, 0.04, 0.06 and 0.10 mg/L. The NH_4^+ concentration was determined *via* spectrophotometry using the classical Nessler method (Krug et al., 1979), the detection limit of NH_4^+ ions was 0.02 mg/L. The concentrations of major cations (including K^+, Na^+, Ca^{2+}, and Mg^{2+}) were determined *via* inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Scientific IRIS Intrepid-II system, the detection limits of K^+, Na^+, Ca^{2+}, and Mg^{2+} ions were 0.01, 0.03, 0.04, and 0.01 mg/L. In addition, the concentrations of Al^{3+} and Sr^{2+} were measured *via* inductively coupled plasma mass spectrometry (ICP-MS) using a VG POEMS III system in the State

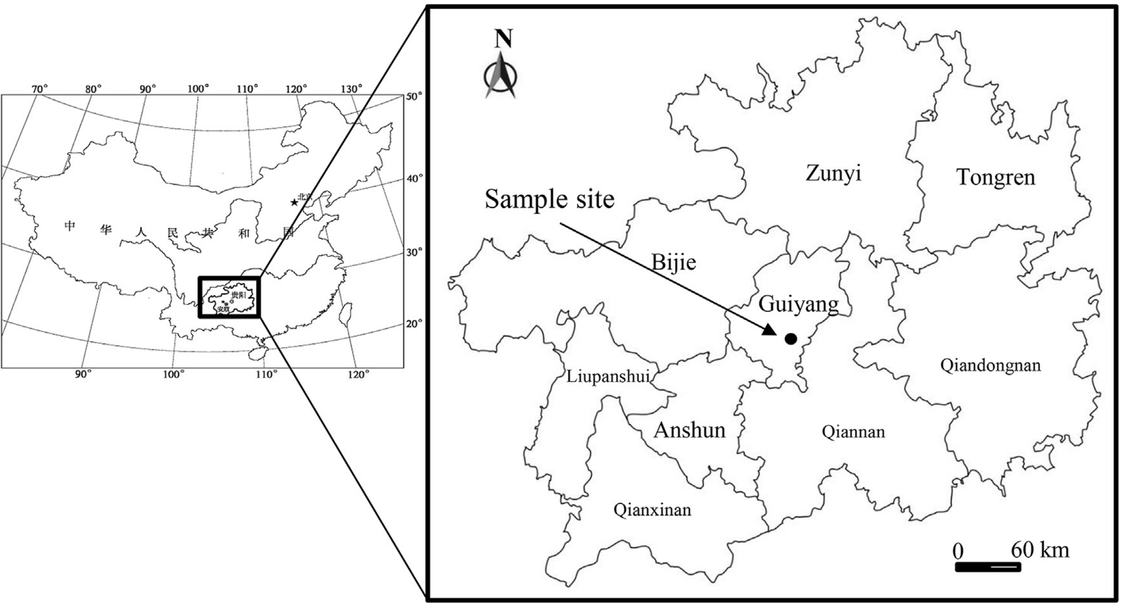

Fig. 1. A sketch map showing the location of Guiyang city, southwest China.

Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan), China. All blanks of the measured species were below the detection limits, and repeated analyses of standards suggest that relative analytical errors in all cases were less than ± 5%.

For each ion species, the volume-weighted mean (VWM) concentrations (pH or ion concentration) were calculated using the following formula:

$$XVWM = \frac{\sum_{i=1}^{n} X_i P_i}{\sum_{i=1}^{n} P_i} \tag{1}$$

where P_i is the volume of the ith rainwater sample (in millimeters) and X_i is the concentration of the species (μmol/L) in the water sample (Sequeira and Lai, 1998; Rao et al., 2017).

3.2. Analytical technique for Ca isotope composition

The Ca isotope composition was measured using the double spike method described by Heuser et al. (2002). The ^{43}Ca–^{48}Ca double spikes were added to each sample prior to chemical purification. In the mixtures, most ^{43}Ca and ^{48}Ca are derived from the spikes, while the bulk of ^{40}Ca and ^{44}Ca comes from the samples. Thus, based on the measured ^{40}Ca/^{48}Ca and ^{44}Ca/^{48}Ca ratios and the ^{43}Ca/^{48}Ca ratio in the spike, we can correct for Ca isotope fractionation during chemical purification and instrumental mass-bias during analysis by a mass spectrometer (Heuser et al., 2002). During chemical purification, water samples containing Ca were first dried down, and then dissolved in ~1.5 N HCl before being passed through a cation exchange column filled with resin (MCI-Gel, 75–150 μm). The purified mixture of ~300 ng Ca sample and spike was dried and then dissolved in ~1 μl 2.2 N HCl before being loaded, along with a $TaCl_5$-activator solution using the "sandwich-technique" activator-sample-activator, onto a previously out-gassed single filament (made of zone-refined rhenium). After the filament was dried, the electric current was increased until the filament ribbon glowed red. The calcium isotope ratios were then determined using a Triton T1 thermal ionization mass spectrometer (TIMS, ThermoFisher, Bremen, Germany) at GEOMAR (Helmholtz Centre for Ocean Research, Germany) following the method described by Heuser et al. (2002). Data acquisition was performed in two steps, as this mass spectrometer is unable to cover the full mass range between 40 and 48 atomic mass units (amu) at once. In the first step, ^{40}Ca, ^{42}Ca, ^{43}Ca, and ^{44}Ca were measured. In the second step, ^{43}Ca and ^{48}Ca were measured simultaneously. During data acquisition, ^{41}K was monitored continuously to correct for isobaric interferences on mass 40, although the correction is negligible. The signal intensity during acquisition typically ranged between 7 V and 9 V for ^{40}Ca. For each sample, six blocks of 20 cycles (corresponding to 120 single scans) were measured.

The isotopic composition of Ca is expressed using $\delta^{44/40}$Ca notation as follows:

$$\delta^{44/40}Ca = \left[\frac{(^{44}Ca/^{40}Ca)_{sample}}{(^{44}Ca/^{40}Ca)_{SRM915a}} - 1 \right] \times 1{,}000 \tag{2}$$

where SRM915a is the international Ca isotope standard (Eisenhauer et al., 2004). The precision of our measurements was expressed as two standard deviations (2SD) of the mean values determined by repeated sample measurements. In a session, the typical 2 SD for the repeated measurement of standard SRM915a was ± 0.09‰ ($n = 4$). Over the course of this study, the mean ^{44}Ca/^{40}Ca value for SRM915a was determined to be 0.021182 ± 0.000006 (2SD, $n = 36$), while the total Ca in blank samples was less than 2 ng (ca. 0.7%). A fluorite (CaF_2) standard was measured during the measurement to have $\delta^{44/40}$Ca = 1.41 ± 0.01‰ ± (2SD, $n = 9$).

3.3. Analytical methods of Sr isotope composition

Following the procedure by Krabbenhoft et al. (2009), samples containing between 1500 and 3000 ng of Sr were split into two aliquots, one of which was mixed with ^{87}Sr–^{84}Sr double spikes to enable the measurement of $\delta^{88/86}$Sr. The pure Sr fraction was extracted from the spiked or unspiked aliquot using a chromatographic column filled with 200–300 μl of Eichrom Sr-Specific resin. Samples were loaded and washed with 8 N HNO_3, and Sr was eluted with 6 ml ultrapure H_2O (18.2 MΩ cm at 25 °C). Following separation, samples were dried in Teflon beakers and heated at 120 °C for several hours with a 1:1 mixture of HNO_3 (65%) and H_2O_2 (30%) to remove resin residuals. Finally, samples were dried again and about 450 ng of Sr were loaded with H_3PO_4 and $TaCl_5$ activator onto rhenium filaments.

All isotopic analyses were carried out at GEOMAR using the Triton T1 system (*cf.* Section 3.2). Before acquiring sample data, the baseline was recorded and amplifier rotation was performed. During the analysis, ^{85}Rb was continuously monitored to detect the possible interference of ^{87}Rb on ^{87}Sr. Data were acquired at a typical signal intensity of ~6 V at ^{88}Sr, requiring an average filament temperature of ~1450 °C. For each sample, nine blocks of 14 cycles (corresponding to 126 single scans) were measured. When using the double-spike technique, data in the first and last blocks were normalized to the mean ^{87}Sr/^{84}Sr ratio from the first block. The spike-correction and normalization of results were carried out following Krabbenhoft et al. (2009). Variations in ^{88}Sr/^{86}Sr were reported as follows:

$$\delta^{88/86}Sr\,(‰) = \left[\frac{(^{88}Sr/^{86}Sr)_{sample}}{(^{88}Sr/^{86}Sr)_{SRM987}} - 1\right] \times 1{,}000 \quad (3)$$

Radiogenic ^{87}Sr/^{86}Sr ratios were determined using the Sr solution purified from the unspiked solution and the instrumental mass-bias was corrected by choosing the internationally-accepted ^{88}Sr/^{86}Sr value of 8.375209. The measurement of the standard (NIST SRM987) showed an average ^{87}Sr/^{86}Sr of 0.710256 ± 0.000028 (2σ, $n = 64$). The seawater standard (IAPSO) was processed and measured using the same procedures as our samples to monitor the column chemistry and the stability of mass-spectrometers. Over the course of our analysis, the ^{87}Sr/^{86}Sr value of IAPSO was 0.709174 ± 0.000012 (2σ, $n = 9$) and $\delta^{88/86}$Sr value of IAPSO was 0.389 ± 0.007‰ (2σ, $n = 9$).

4. Results

4.1. Major ion concentrations of rainwater samples

Concentrations of major cations and anions, stable Ca isotope compositions, as well as radiogenic and stable Sr isotope compositions are presented in Table S1. Volume-weighted mean (VWM) values of ion concentrations from rainwater samples and related statistical analyses are presented in Table 1. The ion charge balance is an indicator of completeness of the measured major constituents (Al-Khashman, 2005). The average correlation coefficients between the sum of anions and the sum of ctions (TZ^-/TZ^+) was about 0.84 for the rainwater samples, indicating that almost ions were measured. The anion deficiency might be due to unmeasured organic anions in samples.

Pure water in equilibrium with an unpolluted atmosphere containing CO_2, NO_x and SO_2 is slightly acidic with a pH = 5.0–5.6 (Charlson and Rodhe, 1982). Thus, natural acidity is defined as pH of 5.6, and precipitation with a pH < 5.0 is normally classified as acid rain (Drever, 1997). In our measurements, pH values of rainwater samples ranged from 4.2 to 8.0 (VWM = 6.2). About 80% of the samples tested in this study had pH > 5.0, indicating the input of alkaline substances into precipitation (Xu and Han, 2009). Moreover, the decreasing order of cation and anion abundances in the precipitation was $Ca^{2+} > NH_4^+ > Mg^{2+} > Na^+ > K^+$; $SO_4^{2-} > NO_3^- > F^- > Cl^-$. The VWM concentration of Ca^{2+} is ~175 μmol/L, accounting for about 70% of the total cations. Previous studies suggested that HCO_3^- is significantly present in the higher pH ranges (pH > 5.5), but can be neglected in lower pH ranges (Noguchi et al., 1995). In this work, even at pH > 5.5, we still could not measure any HCO_3^-. To the exclusion of HCO_3^-, SO_4^{2-} and NO_3^- were the two

Table 1
Volume-weighted mean pH value and ion concentrations (in μmol/L) of rainwater.

Species	VWM	Mean	Median	S.D.	Min	Max
pH	6.2	6.1	6.3	1.1	4.2	8.0
F^-	19.9	28.1	17.3	32.2	0.0	175.1
Cl^-	5.7	10.6	6.7	12.0	0.0	52.9
NO_3^-	26.1	51.4	17.4	86.2	0.0	444.0
SO_4^{2-}	137.3	240.9	143.3	326.6	5.2	2018.8
NH_4^+	35.4	55.9	36.0	65.8	0.0	350.7
Na^+	10.9	17.0	10.6	29.0	1.7	197.5
Mg^{2+}	31.1	40.2	31.5	30.8	5.1	132.9
K^+	10.2	14.4	9.1	15.4	2.4	84.6
Ca^{2+}	174.7	270.7	195.9	285.3	21.4	1630.5
Al^{3+}	3.8	4.6	3.6	3.9	0.2	13.1
Sr^{2+}	0.2	0.3	0.2	0.4	0.0	1.8

Note: VWM is the volume-weighted mean, whereas the rest is the arithmetic mean, median, one standard deviation (S.D.), minimum (Min) and maximum (Max) of the measured result.

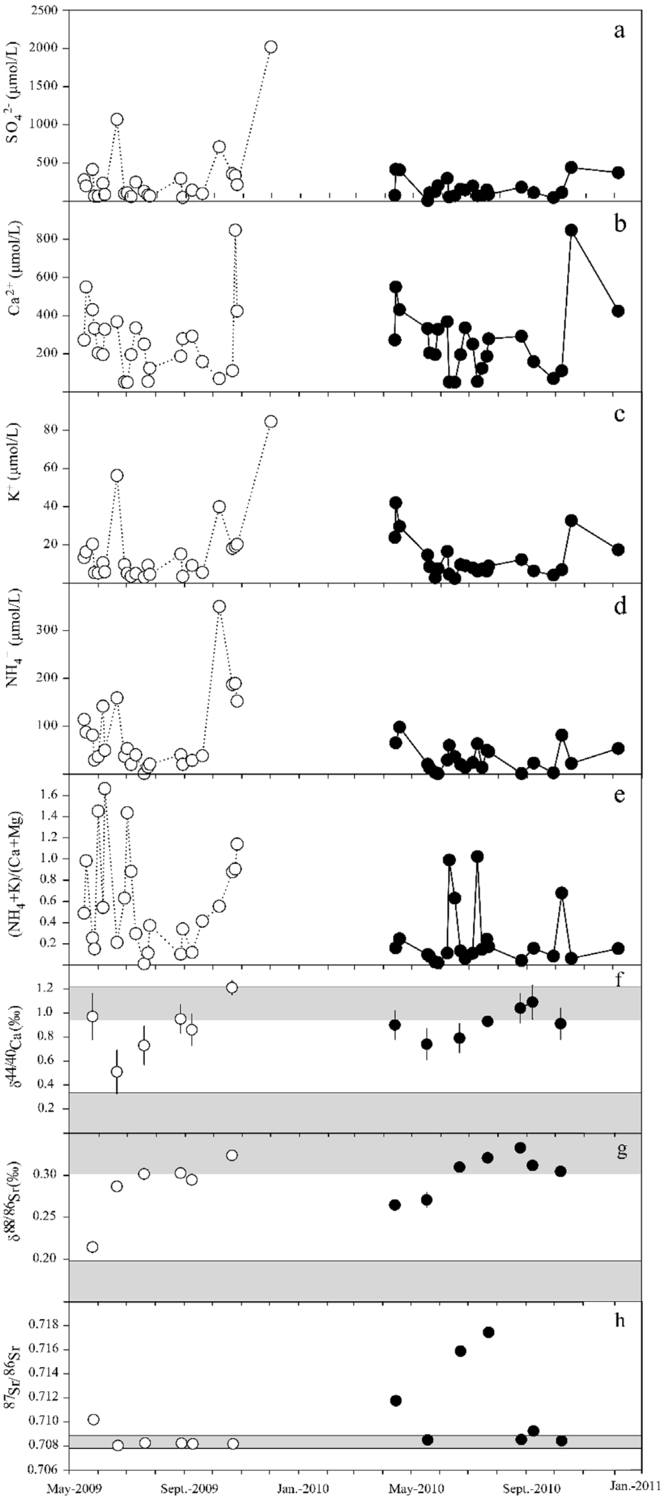

Fig. 2. The temporal variation of the concentrations of SO_4^{2-}, Ca^{2+}, K^+, NH_4^+, $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$ molar ratios, $\delta^{44/40}$Ca, $\delta^{88/86}$Sr and ^{87}Sr/^{86}Sr ratios of the rainwater from Guiyang city. The hollow circle showed the rainwater samples collected in 2009 and the solid circle showed the rainwater samples collected in 2010.

dominant anions, accounting for 73% and 14% of total anions, respectively.

The concentrations of SO_4^{2-}, Ca^{2+}, K^+ and NH_4^+ between May 2009 and December 2010 are depicted in Fig. 2a–d. The plots show two prominent features. First, in both years, the concentrations and isotopic ratios (including $\delta^{44/40}$Ca, ^{87}Sr/^{86}Sr, and $\delta^{88/86}$Sr) were higher in late spring to early summer (e.g., in June of 2009, April and May of 2010), than in the summer months (July–October). They were also elevated in mid-fall to early-winter (October–December). Second, on average the concentrations of these ions were lower in 2010 than in 2009. These variations reflect the seasonal variations in sources of atmospheric aerosols and their contributions to rainwater. They will be further discussed in section 5.5.

4.2. *Ca and Sr isotope ratios*

Our results show that rainwater samples from the city of Guiyang are enriched in light ^{40}Ca relative to seawater (1.88‰, for example De La Rocha and DePaolo, 2000). They have $\delta^{44/40}$Ca values ranging between 0.51‰ and 1.21‰ (Table S1). These values are slightly higher than those measured in European cities (0.27‰ −1.01‰, Schmitt and Stille, 2005). The $\delta^{44/40}$Ca values of precipitation in July and August are higher than those in the other months (Fig. 2).

^{87}Sr/^{86}Sr ratios of Guiyang rainwater range from 0.70800 to 0.71742 (Table S1). These values are like those previously reported by Han and Liu (2006, varied from 0.707934 to 0.709080) and Han et al. (2011, varied from 0.707684 to 0.710094). Significantly-higher ^{87}Sr/^{86}Sr ratios can also be noted between June 2010 and July 2010 (Fig. 2).

The $\delta^{88/86}$Sr values of the rainwater samples range between 0.215‰ and 0.333‰ (Table S1), with a mean value of 0.296‰. All measured $\delta^{88/86}$Sr values for rainwater samples are lower than those for seawater (~0.39‰; Krabbenhoft et al., 2010). This is consistent with the compositions measured for other rainwater samples (Pearce et al., 2015a,b).

5. Discussion

5.1. *Alkalization of rainwater from Guiyang city*

The concentrations of major ions and the pH values of the rainwater samples can be compared with data available from Guiyang between 1999 and 2008, and other regions of China (Table 2). Between 1999 and 2008, rainwater samples from Guiyang city were predominantly made up of acid precipitation ($pH < 5.0$), similar to some other major cities of China, except Lanzhou. From 2008 to 2011, the pH value of rainwater from Guiyang city increased by about 1.2 units, for the same interval the concentrations of SO_4^{2-} and NO_3^- were reduced by almost half (from 129 μmol/L to 69 μmol/L, and from 40 μmol/L to 26 μmol/L, respectively). The content of Ca^{2+} was reduced by 1/5 (from 109 μmol/L to 88 μmol/L). These significant changes (the concentrations of acid ions decreased sharply and the concentrations of alkaline ions decreased less) can be qualitatively explained by two factors. First, Guiyang city is underlain by carbonate and facing rapid urbanization and municipal construction. Carbonate dusts raised into the atmosphere results in increased pH value because of the soil dust (including carbonate and silicate) helps to neutralize rainwater acidity (Xu et al., 2009). Second, since 2008, the Ministry of Ecology and Environment of China (MEE), formally known as State Environmental Protection Administration (SEPA) before 2008, tightened restrictions on SO_2 emissions, which helped to reduce the SO_4^{2-} concentrations in rainwater.

Previous studies have indicated that the Ca^{2+} in Guiyang rainwater is predominantly derived from natural sources, including carbonate and silicate dusts and anthropogenic pollution such as fertilizer, municipal construction, cement factories, and the combustion of coal (Han and Liu, 2006; Han et al., 2011). In the following section, Ca and Sr isotope compositions of rainwater from Guiyang city are used to constrain these sources, their mixing relationships, and their seasonal variations between 2009 and 2011.

5.2. *Sea salt contribution to rainwater chemistry*

The chemical composition of rainwater might be affected by sea salts, crustal and volcanic dusts, biogenic materials, and anthropogenic inputs (e.g., Roy and Negrel, 2001; Negrel et al., 2007). To help evaluate and correct for the contribution of a given element from sea salt, sodium is frequently used as the reference element; chlorine can sometimes be used if the Cl^-/Na^+ ratio of rainwater does not differ significantly from that of seawater (Negrel and Roy, 1998). In this work, we followed the established procedure (Negrel and Roy, 1998; Schmitt and Stille, 2005; Negrel et al., 2007), comparing the element-to-Na ratios in rainwater to those in seawater to remove the contribution of sea salt. First, the terrestrial Na (Na_t) in our rainwater samples can be calculated by assuming a constant terrestrial $(Na/Al)_t$ ratio of 0.11, following Hofmann et al. (1977) and Negrel and Roy (1998):

$$Na_t = Al_{rw} \times 0.11 \tag{4}$$

where Al_{rw} is the concentration of aluminum (Al) in the rainwater. The proportion of sea salt and terrestrial end-members can be calculated using Na as the marine reference species as follows:

$$Na_{ref} = Na_{rw} - Na_t = Na_{rw} - 0.11 \times Al_{rw} \tag{5}$$

Finally, the concentration of a given element X from a terrestrial source (i.e., $X = Cl^-$, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, and Sr^{2+}) can calculated as follows:

$$X_t = X_{rw} - Na_{ref} \times (X/Na)_{sw} \tag{6}$$

Due to the low concentrations of Al in our samples (Al_{rw} = 0.2–13.1 μmol/L), the calculated contribution from marine sources is less than 2% of the total ions; this result is consistent with previous studies, which shows that SO_4^{2-}, Ca^{2+}, and Sr^{2+} of Guiyang rainwater are dominantly derived from non-sea salt sources (e.g. Han

Table 2

Comparison of the major ion concentrations (μeq/l) and pH values in Guiyang city with other sites in China.

Site	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	Date	references
Guiyang (VWM)	6.2	19.9	5.7	26.1	137.3	35.4	10.2	10.9	174.7	31.1	2009–2011	This study
Guiyang (VWM)	4.9	14.3	9.8	39.6	237.8	77	11.1	1.8	217.6	18.6	2007–2008	Han et al. (2011)
Guiyang (Mean)	4.5		21.2	48.2	188		11	4	113.2	25.2	1999–2001	Han and Liu (2006)
Beijing (VWM)	5.12	15.7	104	109	316	186	17.7	25	607	40.4	2006	Xu and Han (2009)
Shanghai (VWM)	4.49	11	58.3	49.8	199.6	80.9	14.9	50.1	204	29.6	2005	Huang et al. (2008)
Nanjing (VWM)	5.51		143	39.6	242	193	12.1	23	295	31.7	1992–2003	Tu et al. (2005)
Chengdu (VWM)	5.1	6.2	8.9	156.2	212.8	150.5	6.6	1.4	196.6	16.2	2008	Wang and Han (2011)
Chengdu (VWM)	4.4		42.3	30.4	431.5	250.7	20.8	22.6	192	33.2	1989	Lei et al. (1997)
Chongqing (VWM)	4.6		40.3	43.2	421.8	386.6	15.2	39.8	207.2	13.2	1989	Lei et al. (1997)
Lanzhou(VWM)	7.7	13.6	27.9	74.4	208	57.2	7.26	12.3	886	46.5	2007	Xu et al. (2009)
South of China (mean)	4.41		16.3	28.2	166.3	61.7	10.8	11.3	82.1	21.5	2001–2003	Aas et al. (2007)

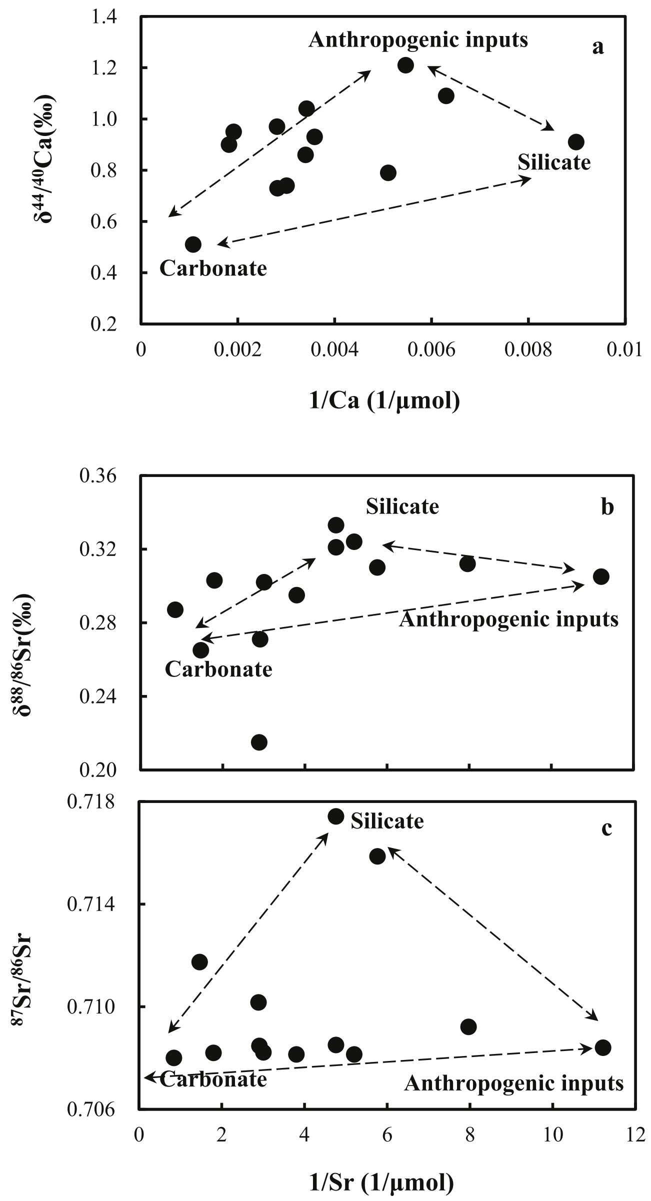

Fig. 3. Variation of isotopic ratios versus 1/Ca and 1/Sr molar ratios in the rainwater samples.

and Liu, 2006; Han et al., 2011). Thus, we ignored the contribution of sea salts in the following discussion.

5.3. *Identifying the sources of Ca and Sr ions in rainwater*

As Ca is a major cation in rain water and is present in the main aerosol reservoirs, the isotopic composition of Ca can be used to trace the sources of aerosols. In a plot of $\delta^{44/40}$Ca against 1/Ca (the inverse of Ca concentration in μmol/L), the mixtures of two geochemical reservoirs sit on a line (Langmuir et al., 1978). Fig. 3a shows that our data can be qualitatively explained by the mixing of at least three components of Ca in the rainwater: one component (C) characterized by a high Ca abundance but a low $\delta^{44/40}$Ca ($\sim$0.5‰), one component (S) characterized by a relatively low Ca concentration and an intermediate $\delta^{44/40}$Ca ($\sim$0.8‰), and one component (A) characterized by an intermediate Ca concentration but the highest $\delta^{44/40}$Ca ($\sim$1.2‰). By Comparing these concentrations with the Ca concentrations and isotope compositions of known reservoirs (Table 3), we can conclude that components S and C are most likely to be silicate and carbonate dusts, respectively (possibly sourced from local and distant continental bedrocks and soil dusts). Ryu et al. (2011) found that Ca isotope variation during granite weathering could be quantitatively linked to the dissolution of individual, Ca-bearing minerals having distinctive Ca isotope signatures by using a column reactor. Fantle and Tipper (2014) suggested that the mean $\delta^{44/40}$Ca value of carbonate rocks is $\sim$0.60‰, and Holmden and Belanger (2010) reported the $\delta^{44/40}$Ca value of silicates ranging from 0.61‰ to 1.00%. It is also well-known that carbonates have a much higher Ca concentration and higher solubility in water than most silicate dusts.

Similarly, the relationship between ^{87}Sr/^{86}Sr or $\delta^{88/86}$Sr and 1/Sr (the inverse of the Sr concentration in μmol/liter) requires the mixing of three components (Fig. 3b and c). Based on the known Sr reservoirs (Table 3), the component with high ^{87}Sr/^{86}Sr ($\sim$0.717) and high $\delta^{88/86}$Sr ($\sim$0.32‰) with intermediate amounts of Sr is more likely to be silicate soil dust, whereas the component with low ^{87}Sr/^{86}Sr ($\sim$0.708) and low $\delta^{88/86}$Sr ($< \sim$0.26‰) with a high concentration of Sr is more likely to be carbonate soil dust. These two end-members have Sr isotope characteristics comparable with those previously reported by Pearce et al. (2015a, b). For example, the Parisian rainwater has ^{87}Sr/^{86}Sr = 0.708–0.711 and $\delta^{88/86}$Sr = 0.16‰–0.31‰. Although there are no reported data on the isotopic signatures of local anthropogenic reservoirs, some studies of these potential reservoirs (summarized in Table 3) hint that a third end-member of atmospheric aerosols, having the highest $\delta^{44/40}$Ca and intermediate 1/Ca in Fig. 3a and intermediate $\delta^{88/86}$Sr and ^{87}Sr/^{86}Sr with low Sr concentration in Fig. 3b and c, is likely to be sourced from various anthropogenic sources including fertilizer, automobile exhaust, and coal-burning for heating or power-plant. For example, Negrel and Deschamps (1996) reported that the ^{87}Sr/^{86}Sr ratio of fertilizer from France ranged from 0.7079 to 0.7087. Negrel et al. (2007) reported that the ^{87}Sr/^{86}Sr ratios of aerosols from automobile exhaust varied between 0.7077 and 0.7083, ratios of aerosols from urban heating varied between 0.7083 and 0.7335, and ratios of aerosols from incinerators varied between 0.7097 and 0.7100 in the air of Paris. Pearce et al. (2015a, b) reported $\delta^{88/86}$Sr ratios of about 0.24‰ − 0.48‰ for fertilizer.

Since the typical fertilizers used in southwestern China include carbamide, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, KH_2PO_4, and K_2SO_4, the addition of Ca^{2+} and Sr^{2+} ions in rainwater from fertilizer should be accompanied by increased concentrations of K^+ and $NH_4{}^+$. Plants are also likely to serve as a source of non-sea salt Ca and Sr in precipitation (Nakano and Tanaka, 1997; Nakano et al., 2006). Ca, Sr and K can be leached out of ashes produced by slash-and-burn agriculture (burning plants for potash during winter) or from coal-burning by rainwater. Ca and Mg in rainwater are mostly derived from dissolution of silicate and carbonate dusts. Thus, the $(K^+ + NH_4{}^+)/(Ca^{2+} + Mg^{2+})$ molar ratio is used as a chemical index in this study to further evaluate the relative contributions of anthropogenic source (e.g., fertilizer and plant or coal burning) and terrestrial sources. Note that one complication associated with coal-burning is the release of $SO_{2,}$ as well as ashes. The neutralization of dissolved SO_2 by carbonate and silicate aerosols would also increase the contribution of Ca and Sr from terrestrial sources.

In Fig. 4a–c, $(K^+ + NH_4{}^+)/(Ca^{2+} + Mg^{2+})$ is plotted against $\delta^{44/40}$Ca, $\delta^{88/86}$Sr and ^{87}Sr/^{86}Sr, respectively. Again, our data require the mixing of at least three components: a silicate component where $\delta^{44/40}$Ca = $\sim$0.8‰, $\delta^{88/86}$Sr $\geq \sim$0.34‰, and ^{87}Sr/^{86}Sr $\geq \sim$0.717, a carbonate component where $\delta^{44/40}$Ca = $\sim$0.5‰, $\delta^{88/86}$Sr $\leq \sim$0.26‰ and ^{87}Sr/^{86}Sr $\leq \sim$0.7080, and an anthropogenic component exhibiting high $(K^+ + NH_4{}^+)/(Ca^{2+} + Mg^{2+})$ values. From these plots, we can infer that the anthropogenic components exhibit $\delta^{44/40}$Ca $\geq \sim$1.2‰, $\delta^{88/86}$Sr = $\sim$0.30‰ and ^{87}Sr/^{86}Sr = $\sim$0.7080. These Ca and Sr isotope signatures of the anthropogenic component are also consistent with the third component (besides carbonate and silicate aerosols) in Fig. 3a–c, which suggests that it is an anthropogenic component containing low concentrations of Sr but intermediate levels of Ca.

In the $\delta^{44/40}$Ca-$\delta^{88/86}$Sr–^{87}Sr/^{86}Sr space (Fig. 5), our rainwater

Table 3
Characteristic isotope ratios of the end-members in the rainwater.

Items	$^{87}Sr/^{86}Sr$	$\delta^{88/86}Sr$(‰)	$\delta^{44/40}Ca$ (‰)	Reference
Seawater	0.70917	0.389	1.88	$^{87}Sr/^{86}Sr$ data come from Schmitt et al. (2003); $\delta^{44/40}Ca$ data come from De La Rocha and DePaolo (2000)
Global statistics				
Carbonate rocks ($n = 1301$)			~0.6	Fantle and Tipper (2014)
Silicate rocks ($n = 153$)			0.94	Fantle and Tipper (2014)
rain and dust ($n = 60$)			0.72	Fantle and Tipper (2014)
Plant ($n = 163$)			0.01	Fantle and Tipper (2014)
River ($n = 259$)			0.88	Fantle and Tipper (2014)
Global rain water	0.707–0.715	0.12–0.25	−1.31–1.01	$^{87}Sr/^{86}Sr$, $\delta^{44/40}Ca$ data come from Schmitt et al.(2003; 2005); $\delta^{88/86}Sr$ data come from Hinshaw et al.(2014)
Boreal rivers of Canada	0.713–0.734	0.27–0.39		Stevenson et al. (2018)
Dissolved load in glacier flow	0.710–0.711	0.26–0.40		Stevenson et al. (2016)
Suspended sediment in glacier flow	0.708–0.730			Stevenson et al. (2016)
Rainwater from Paris	0.708–0.711	0.16–0.312		Pearce et al. (2015a,b)
Silicate rocks			0.6–1.0	Holmden and Belanger (2010)
Anthropogenic inputs	0.708–0.734			Negrel et al.(2007)
River water in southwestern of China				
River water(limestone)	0.7075			Han and Liu (2004)
River water(dolomite)	0.711			Han and Liu (2004)
River water(silicate)	> 0.715			Han and Liu (2004)
Isotopic signature of aerosols inferred from Guiyang Rain water				
Silicate aerosol (end member)	≥0.717	≥ ~0.34	~0.8	This study
Carbonate aerosol(end member)	≤ ~0.708	≤ ~0.32	~0.5	This study
Anthropogenic sources	~0.708	~0.30	≥ ~1.2	This study

samples can be explained by the mixing of ions from three prominent sources: dissolution of carbonates (low $\delta^{44/40}Ca$, $\delta^{88/86}Sr$, and $^{87}Sr/^{86}Sr$), dissolution of silicates (intermediate $\delta^{44/40}Ca$, high $\delta^{88/86}Sr$, and $^{87}Sr/^{86}Sr$), and an anthropogenic component (high $\delta^{44/40}Ca$, low $\delta^{88/86}Sr$, and $^{87}Sr/^{86}Sr$). This finding is consistent with the relationships depicted in Figs. 3 and 4. Moreover, it shows that the $\delta^{44/40}Ca$ ratios are lower than those of seawater. This indicates the dominance of terrestrial sources for carbonate minerals, as well as anthropogenic inputs. In addition, the congregation of our data towards carbonate weathering and anthropogenic inputs (Figs. 3–5) indicates that these two components are the most important inputs into rainwater in Guiyang city. However, it remains uncertain if this means that the densities of atmospheric silicate aerosols are much lower than those of carbonate and anthropogenic aerosols. This is because silicate aerosols typically have much lower solubility in rainwater than the other two sources.

5.4. Identifying sources of other ions in rainwater

Under the framework established by Ca and Sr isotope compositions, the origins of other ions in rainwater can be identified by conducting cross-correlation and principle component analyses.

Correlation coefficients between ionic species in rainwater are shown in Table 4. Our results suggest a lack of correlation between pH and NO_3^- or SO_4^{2-}, which makes sense, given that NO_3^- and SO_4^{2-} in rainwater are neutralized as salts (e.g. NH_4NO_3 or $CaSO_4$) rather than being charge-balanced by hydrogen ion (e.g., HNO_3, H_2SO_4 or HSO_4^-). In contrast, concentrations of K^+ and Ca^{2+} are closely correlated with SO_4^{2-} ($R = 0.93$ and 0.91, respectively). K^+ is also closely-correlated with Ca^{2+} ($R = 0.90$), suggesting that some Ca^{2+} ions could come from K_2SO_4 fertilizer. It can be seen that the F^- is higher than those of Cl^- in Table S1. The relative high correlations with other ions (SO_4^{2-}, Cl^-, Ca^{2+}, and K^+, Table 4) indicate the common sources of these elements as fly ash and glue gases of coal burning in power plants and domestic heating (Brueggemann and Rolle, 1998).

A varimax-rotated principal component analysis (PCA) was conducted using SPSS 16.0 to reveal the relationships among all measured ions and isotopic compositions and to help further determine the source apportionment of the chemical species measured in the rainwater. Before PCA analysis, a normalization was conducted on each chemical index by removing the average value and then dividing it by its standard deviation. This was done to reduce the discrepancies caused by different ranges of chemical indices. The results of PCA analysis are shown in Table 5 and Fig. 6. The three main principle components with highest eigenvalues were extracted; they account for 78.8% of the variance. The first principle component (PC1) explains ~52.0% of the total variance. Table 5 and Fig. 6 show that PC1 increases with increasing concentrations of Na^+, K^+, Ca^{2+}, SO_4^{2-}, Cl^-, NH_4^+, Mg^{2+}, Sr^{2+}, and decreasing values of $\delta^{44/40}Ca$ and $\delta^{88/86}Sr$. The significant covariations of the 8 concentrations originated mainly from the charge balance—the majority of anions, including SO_4^{2-} and Cl^-, were charge-balanced by cations including Ca^{2+}, NH_4^+, Mg^{2+}, Na^+, K^+, and Sr^{2+}. The significant covariations of these concentrations with $\delta^{44/40}Ca$ and $\delta^{88/86}Sr$ have been explained by correlations between $\delta^{44/40}Ca$ versus 1/Ca and $\delta^{88/86}Sr$ versus 1/Sr attributable to the mixing of various ion-sources including the dissolution of carbonate and silicate aerosols, and anthropogenic inputs (as explained in section 5.2).

The second principle component (PC2) accounts for ~15.6% of the total variance and increases with increasing NO_3^-, $^{87}Sr/^{86}Sr$ and decreasing pH and F^-. When the charges of major ions are balanced, the pH values of rainwater are controlled by pCO_2 as well as some minor components such as F^- and NO_3^- that are probably not balanced by alkaline and silicate aerosols (Charlson and Rodhe, 1982). For example, fluorine could be released as HF, SiF_4, and CF_4 during coal combustion (Liu et al., 2007), which could affect the pH value of rainwater. The significant negative covariations of pH and $^{87}Sr/^{86}Sr$ (PC2 = 0.68) can also be explained by the differential contributions of silicate and carbonate aerosols due to the changes in the pH value of solution as follows: 1) the dissolution of carbonate minerals will result in a high pH value, and relative low $^{87}Sr/^{86}Sr$ value (Goldstein and Jacobsen, 1987); 2) at low pH values, the contribution from the dissolution of silicate aerosols may dominate (due to either high concentrations of Sr in silicate aerosols and/or high densities of silicate aerosols in atmosphere), resulting in higher $^{87}Sr/^{86}Sr$ values (e.g., Gaillardet et al., 1999). The third principle component (PC3) accounts for ~11.2% of the total variance; it increases with increasing Al^{3+}. In summary, the three principle components can be explained by the mixing of three major sources, including dissolution of carbonate aerosol, dissolution of silicate aerosol, and anthropogenic inputs; these finding are consistent

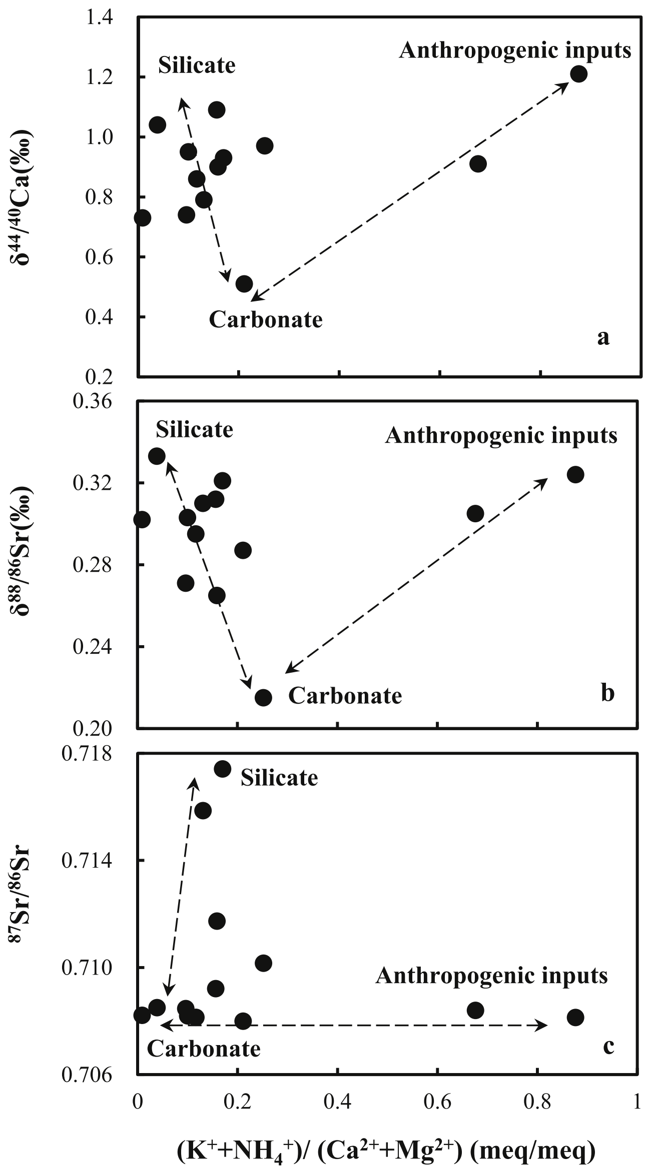

Fig. 4. Variation of isotopic ratios versus $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$ molar ratios in the rainwater samples.

with constraints posed by Ca and Sr isotope compositions of rainwater.

5.5. Seasonal variation of the atmospheric aerosols

The elemental concentrations and isotopic compositions of rainwater from Guiyang city can be explained by the mixing of at least three major reservoirs: (1) the carbonate aerosol source characterized by low $^{87}Sr/^{86}Sr$, $\delta^{88/86}Sr$ and $\delta^{44/40}Ca$, very low $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$, low 1/Ca and 1/Sr; (2) the silicate aerosol source characterized by relative high $^{87}Sr/^{86}Sr$, $\delta^{88/86}Sr$ and $\delta^{44/40}Ca$, very low $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$, low 1/Ca and 1/Sr; and (3) an anthropogenic component containing high $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$ (Figs. 3–5). Among these geochemical indices, the concentrations of cations or anions in rainwater are controlled both by their sources, and by other factors including the density and size of aerosols of carbonates, silicates, and fertilizer in the atmosphere, the amount of precipitation, and changes in pH and temperature which affect the dissolution rates. In this regard, the isotope and elemental ratios of rainwater can be more diagnostic of sources. Nevertheless, using these geochemical characteristics, we can evaluate, at least qualitatively, how these sources varied seasonally.

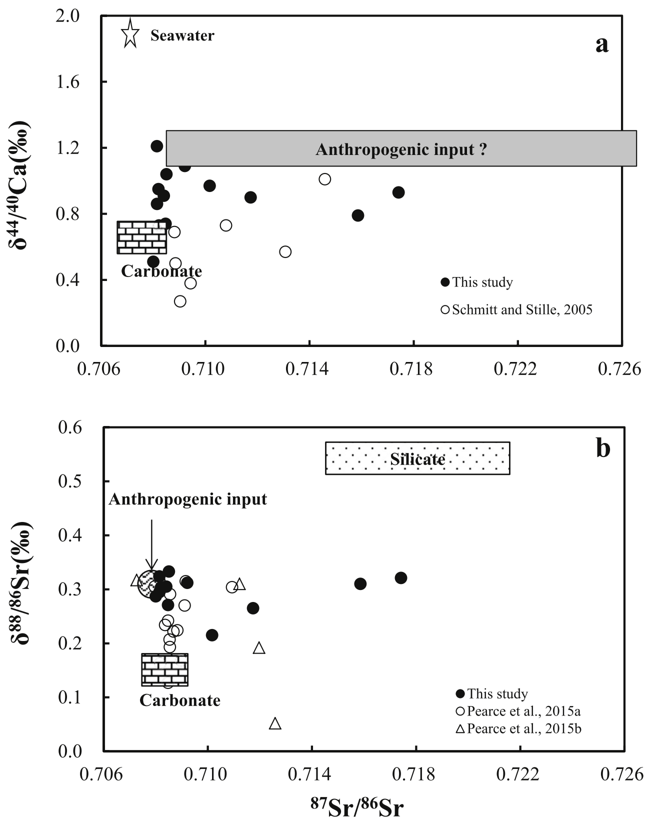

Fig. 5. Variation of $\delta^{44/40}Ca$ and $\delta^{88/86}Sr$ versus $^{87}Sr/^{86}Sr$ in the rainwater samples. The values of the end-members are as bellows: Ca isotopic compositions of carbonates come from De La Rocha and DePaolo (2000)); $\delta^{88/86}Sr$ ratios of carbonates and fertilizer come from Pearce et al. (2015a); $^{87}Sr/^{86}Sr$ ratios of fertilizer come from Negrel et al. (2007).

In Fig. 2, as described in Result 4.3, we can see that the concentrations of SO_4^{2-}, Ca^{2+}, K^+ and NH_4^+ and isotopic ratios (including $\delta^{44/40}Ca$, $^{87}Sr/^{86}Sr$, and $\delta^{88/86}Sr$) are higher in late spring to early summer (i.e., in June of 2009 and April and May of 2010), and mid-fall to early-winter (i.e., October–December) than they are during most summer months (July–October). This feature, to the first order, can be explained by variations in anthropogenic inputs relative to terrestrial inputs; months with geochemical spikes coincide with increased farming activity. For example, fertilizers (including K_2SO_4 and nitrogen fertilizer) are typically applied during the mid-late spring and during the mid-late fall (e.g., in orchards). In mid-fall to early-winter, the burning of plant leaves and stems and/or more coal burning for heating after the harvest may also contribute to chemical anomalies in rainwater. This conclusion can be further confirmed by the higher $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$ ratios observed during these months compared with those observed during the summer months (Fig. 2e). The exact proportions among these anthropogenic sources cannot be extracted until we obtain more information. Moreover, on average, the concentrations of some ions (e.g., SO_4^{2-}, Ca^{2+}, K^+, and NH_4^+) were lower in 2010 than in 2009. This feature, for some ions (e.g., SO_4^{2-}), can be attributed to the reduced anthropogenic inputs in 2010 due to the tightened environmental regulations (as discussed in Section 5.1). However, this feature is also partly caused by the increases in precipitation volume in 2010 and changes in the source of atmospheric aerosols. For example, the dissolution of carbonate aerosols (having higher solubility) appeared to contribute more to rainwater chemistry in 2009 than in 2010, when high $^{87}Sr/^{86}Sr$ ratios indicate more dissolution of silicate aerosols (having lower solubility; Fig. 2h).

Table 4

Matrix of correlation coefficients (*R*) between two ionic concentrations (in μeq/L) in rainwater samples form Guiyang city.

Component	pH	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	Sr^{2+}
pH	1										
NH_4^+	−0.2	1									
K^+	0.07	0.33	1								
Na^+	0.01	−0.04	0.22	1							
Ca^{2+}	0.29	0.10	0.74	0.28	1						
Mg^{2+}	0.01	0.26	0.77	0.23	0.78	1					
F^-	0.23	0.42	0.57	0.27	0.61	0.46	1				
Cl^-	0.00	0.53	0.85	0.21	0.77	0.8	0.66	1			
NO_3^-	0.18	0.34	0.2	0.12	0.27	0.34	0.44	0.31	1		
SO_4^{2-}	0.16	0.24	0.93	0.24	0.91	0.71	0.58	0.82	0.16	1	
Sr^{2+}	0.25	0.41	0.90	0.27	0.97	0.73	0.56	0.74	0.30	0.86	1

Table 5

Results of principle component analyses on thirteen chemical indices of rainwater samples.

	PC1	PC2	PC3
pH	−0.445	**−0.804**	0.071
F^-	0.474	**−0.724**	0.207
Cl^-	**0.890**	0.214	−0.313
NO_3^-	−0.313	**0.575**	0.465
SO_4^{2-}	**0.945**	−0.082	0.242
NH_4^-	**0.796**	0.034	0.390
Na^+	**0.978**	0.121	−0.040
Mg^{2+}	**0.715**	0.315	−0.375
K^+	**0.960**	0.145	0.080
Ca^{2+}	**0.942**	−0.194	−0.028
Al^{3+}	−0.187	0.220	**0.856**
Sr^{2+}	**0.962**	−0.135	0.048
$\delta^{44/40}Ca$	**−0.629**	0.124	−0.446
$\delta^{88/86}Sr$	**−0.517**	−0.268	0.155
$^{87}Sr/^{86}Sr$	−0.244	**0.677**	0.050
Eigenvalue	7.80	2.34	1.68
Variance (%)	51.98	15.59	11.22
Cumulative (%)	51.98	67.57	78.79

6. Conclusions

This study reports the elemental and isotopic compositions of rainwater collected between May 2009 and December 2010 in Guiyang, southwest China. Most rainwater samples are alkaline, with a VWM pH of 6.2; this is consistent with the notion that rainwater acidity may be neutralized by dissolving soil dust. Moreover, both stable ($\delta^{44/40}Ca$ and $\delta^{88/86}Sr$) and radiogenic ($^{87}Sr/^{86}Sr$) isotope compositions of rainwater from the city of Guiyang show variations correlating with the inverse of Sr or Ca concentration as well as $(NH_4^+ + K^+)/(Ca^{2+} + Mg^{2+})$. These variations reflect the relative contributions of anthropogenic inputs to the dissolution of silicate and carbonate aerosols in rainwater. The observed correlations allow us to identify at least three major reservoirs contributing to the rainwater chemistry of Guiyang city. Chemical variations of rainwater between May 2009 and December 2010 can be explained by seasonal farming activities, tightened environmental protection regulations, higher precipitation volumes in 2010, and increased coal-combustion for heating and electricity in winter. Although the verification of these conclusions will require longer continuous, chemical records of rainwater, specially rainwater collected during winter (or the dry season), a quantitative evaluation of these sources will require additional constraints. Nevertheless, our study demonstrates that a combination of elemental compositions, stable Ca and Sr, and radiogenic Sr isotope compositions of rainwater can be used to trace sources of atmospheric aerosols and associated seasonal variations.

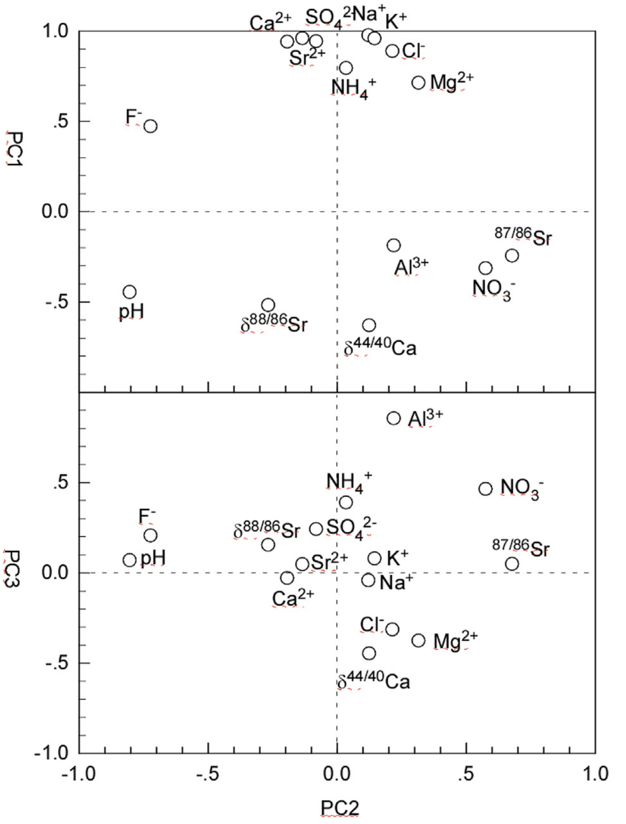

Fig. 6. Principal components analysis of rainwater samples.

Declaration of interest statement

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data

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References

Aas, W., Shao, M., Jin, L., Larssen, T., Zhao, D., Xiang, R., Zhang, J., Xiao, J., Duan, L., 2007. Air concentrations and wet deposition of major inorganic ions at five non-urban sites in China, 2001–2003. Atmos. Environ. 41, 1706–1716.

Aberg, G., Jacks, G., Hamilton, P.J., 1989. Weathering rates and 87Sr/86Sr ratios: an isotopic approach. J. Hydrol. 109, 65–78.

Al-Khashman, O.A., 2005. Ionic composition of wet precipitation in the Petra Region, Jordan. Atmos. Res. 78, 1–12.

Brueggemann, E., Rolle, W., 1998. Changes of some components of precipitation in East Germany after the unification. Water Air Soil Pollut. 107, 1–23.

Charlson, R.J., Rodhe, H., 1982. Factors controlling the acidity of natural rainwater. Nature 295, 683–685.

Chatterjee, J., Singh, S.K., 2012. ^{87}Sr/^{86}Sr and major ion composition of rainwater of Ahmedabad, India: sources of base cations. Atmos. Environ. 63, 60–67.

Chetelat, B., Gaillardet, J., Freydier, R., Negrel, P., 2005. Boron isotopes in precipitation: experimental constraints and field evidence from French Guiana. Earth Planet. Sci. Lett. 235, 16–30.

De La Rocha, C.L., DePaolo, D.J., 2000. Isotopic evidence for variations in the marine calcium cycle over the cenozoic. Science 289 (5482), 1176–1178.

Drever, J.I., 1997. Geochemistry of Natural Waters: Surface and Groundwater Enviromnents, third ed. Prentice hall, New Jersy.

Eisenhauer, A., Nagler, T., Stille, P., Kramers, J., Gussone, N., Bock, B., Fietzke, J., Hippler, D., Schmitt, A.D., 2004. Proposal for an international agreement on Ca notations resulting form discussions at workshops on stable isorope measurements held in Davos (Goldschmidt 2002) and Nice (EGS-AGU-EUG 2003). Geostand. Feoananl. Res. 28, 149–151.

Fantle, M., Tipper, E.T., 2014. Calcium isotopes in the global biogeochemical Ca cycle: implications for development of a Ca isotope proxy. Earth Sci. Rev. 129, 148–177.

Fantle, M.S., Tollerud, H., Eisenhauer, A., Holmden, C., 2012. The Ca isotopic composition of dust-producing regions: measurements of surface sediments in the Black Rock Desert, Nevada. Geochim. Cosmochem. Acta 87, 178–193.

Fietzke, J., Eisenhauer, A., 2006. Determination of temperature-dependent stable strontium isotope (^{88}Sr/^{86}Sr) fractionation via bracketing standard MC-ICP-MS. Geochem. Geophys. Geosyst. 7.

Gaillardet, J., Dupre, B., Allegre, C.J., 1999. Geochemistry of large river suspended sediments: silicate weathering of recycling tracer? Geochim. Cosmochem. Acta 63, 4037–4051.

Goldstein, S.J., Jacobsen, S.B., 1987. The Nd and Sr isotopic systematics of river water dissolved material: implications for the sources of Nd and Sr in seawater. Chem. Geol. 48, 245–272.

Han, G., Liu, C.-Q., 2004. Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. Chem. Geol. 204, 1–21.

Han, G., Liu, C.-Q., 2006. Strontium isotope and major ion chemistry of the rainwaters from Guiyang, Guizhou Province, China. Sci. Total Environ. 364, 165–174.

Han, G., Tang, Y., Wu, Q., Tan, Q., 2010. Chemical and strontium isotope characterization of rainwater in karst virgin forest, Southwest China. Atmos. Environ. 44, 174–181.

Han, G., Wu, Q., Tang, Y., 2011. Acid rain and alkalization in southwester China: chemical and strontium isotope evidence in rainwater from Guiyang. J. Atmos. Chem. 68, 139–155.

Haywood, J., Boucher, O., 2000. Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: a review. Rev. Geophys. 38, 513–545.

Herut, B., Starinsky, B., Katz, A., 1993. Strontium in rainwater from Israel, Sources, isotopes and chemistry. Earth Planet. Sci. Lett. 120, 77–84.

Heuser, A., Eisenhauer, A., Gussone, N., Bock, B., Hansen, B.T., Nagler, T.F., 2002. Measurement of calcium isotopes (δ^{44}Ca) using a multicollector TIMS technique. Int. J. Mass Spectrom. 220, 385–397.

Hofmann, E.J., Hofmann, G.L., Fletcher, I.S., Duce, R.A., 1977. Further consideration of alkali and alkaline earth geochemistry of marine aerosols, results of a study of marine aerosols collected on Bermuda. Atmos. Environ. 89, 149–160.

Holmden, C., Belanger, N., 2010. Ca isotope cycling in a forested ecosystem. Geochim. Cosmochem. Acta 7, 995–1015.

Huang, K., Zhuang, G., Xu, C., Wang, Y., Tang, A., 2008. The chemistry of the severe acidic precipitation in Shanghai, China. Atmos. Res. 89, 149–160.

Krabbenhoft, A., Fietzke, J., Eisenhauer, A., Liebetrau, V., Bohm, F., Vollstaedt, H., 2009. Determination of radiogenic and stable strontium isotope ratios (^{87}Sr/^{86}Sr; $\delta^{88/86}$Sr) by thermal ionization mass spectrometry applying an ^{87}Sr/^{84}Sr double spike. J. Anal. Atomic Spectrom. 24 (9), 1267–1271.

Krabbenhoft, A., Eisenhauer, A., Bohm, F., Vollstaedt, H., Fietzke, J., Liebetrau, V., Augustin, N., Peucker-Ehrenbrink, B., Muller, M.N., Horn, C., Hansen, N.T., Nolte, N., Wallmann, K., 2010. Constraining the marine strontium budget with natural strontium isotope fractionations (^{87}Sr/^{86}Sr*, $\delta^{88/86}$Sr) of carbonates, hydrothermal solutions and river waters. Geochim. Cosmochem. Acta 74, 4097–4109.

Krug, F.J., Ruzicka, J., Hansen, E.H., 1979. Determination of ammonia in low concentrations with Nessler's reagent by flow injection analysis. Analyst 104, 47–54.

Langmuir, C.H., Jr, R.D.V., Hanson, G.N., Hart, S.R., 1978. A general mixing equation with applications to Icelandic basalts. Earth Planet. Sci. Lett. 37 (3), 380–392.

Lei, H.C., Tanner, P.A., Huang, M.Y., Shen, Z.L., Wu, Y.X., 1997. The acidification process under the cloud in southwest China: observation results and simulation. Atmos. Environ. 31, 851–861.

Liu, G., Zheng, L., Duzgoren-Aydin, N.S., Gao, L., Liu, J., Peng, Z., 2007. Health effects of arawnix, fluorine, and selenium from indoor burning of Chinese coal. Rev. Environ. Contam. Toxicol. 89–106.

Lohmann, U., Feichter, J., 2005. Global indiredt aerosol effects: a review. Atmos. Chem. Phys. 5, 715–737.

Ministry of Ecology and Environment of the People's Republic of China, 2017. Bulletin on the State of China's Ecological Environment. http://www.mee.gov.cn/hjzl/zghjzkgb/lnzghjzkgb/.

Nakano, T., Tanaka, T., 1997. Strontium isotope constraints on the seasonal variation of the provenance of base cations in rain water at Kawakami, central Japan. Atmos. Environ. 31, 4237–4245.

Nakano, T., Morohashi, S., Yasuda, H., Sakai, M., Aizawa, S., Shichi, K., Mrisawa, T., Takahashi, M., Sanada, M., Matsuura, Y., Sakai, H., Akama, A., Okada, N., 2006. Determination of seasonal and regional variation in the provenance of dissolved cations in rain in Japan based on Sr and Pb isotopes. Atmos. Environ. 40 7409-7402.

Negrel, P., Deschamps, P., 1996. Natural and anthropogenic budgets of a small watershed in the Massif Central (France): chemical and strontium isotopic characterization in water and sediments. Aquat. Geochem. (2), 1–27.

Negrel, P., Roy, S., 1998. Chemistry of rainwater in the Massif Central (France): a strontium isotope and major element study. Appl. Geochem. 13, 941–952.

Negrel, P., Guerrot, C., Millot, R., 2007. Chemical and strontium isotope characterization of rainwater in France: influence of sources and Hydrogeochemical implications. Isot. Environ. Health Stud. 43 (3), 179–196.

Neymark, L.A., Premo, W.R., Melnikov, N.N., Emsbo, P., 2014. Precise determination of δ^{88}Sr in rocks, minerals,and waters by double-spike TIMS: a powerful tool in the study of geological, hydrological and biological processes. J. Anal. At. Spectrom. 29, 65–75.

Noguchi, I., Kato, T., Akiyama, M., Otsuka, H., Mastxumoto, Y., 1995. The effect of alkaline dust decline on the precipitation chemistry in northern Japan. Water, Air, Soil Pollut. 85.

Pearce, C.R., Parkinson, I.J., Gaillardet, J., Charlier, B.L.A., Mokadem, F., Burton, K.W., 2015b. Reassessing the stable (δ^{88}/^{86}Sr) and radiogenic (^{87}Sr/^{86}Sr) strontium isotopic composition of marine inputs. Geochim. Cosmochem. Acta 157, 125–146.

Pearce, C.P., Parkinson, I.J., Gaillardet, J., Chetelat, B., Burton, K.W., 2015a. Characterising the stable ($\delta^{88/86}$Sr) and radiogenic (^{87}Sr/^{86}Sr) isotopic composition of strontium in rainwater. Chem. Geol. 409, 54–60.

Probst, A., Gh'mari, A.E., Subert, D., Fritz, B., McNutt, R., 2000. Strontium as a tracer of weathering processes in a silicate catchment polluted by acid atmospheric inputs. Strengbach, France. Chem. Geol. 170, 203–219.

Rao, W., Han, G., Tan, H., Jiang, S., 2015. Chemical and Sr isotopic compositions of rainwater on the ordos desert plateau, Northwest China. Environ. Earth Sci. 74, 5759–5771.

Rao, W., Han, G., Tan, H., Jin, K., Wang, S., Chen, T., 2017. Chemical and Sr isotopic characteristics of rainwater on the Alxa Desert Plateau, North China: implication for air quality and ion sources. Atmos. Res. 193, 163–172.

Roy, S., Negrel, P., 2001. A Pb isotope and trace element study of rainwater from the Massif Central (France). Sci. Total Environ. 277, 225–239.

Ryu, J.-S., Jacobson, A.D., Holmden, C., Lundstrom, C., Zhang, Z., 2011. The major ion, $\delta^{44/40}$Ca, $\delta^{44/42}$Ca, and $\delta^{26/24}$Mg geochemistry of granite weathering at pH = 1 and T = 25°C: power-law processes and the relative reactivity of minerals. Geochim. Cosmochem. Acta 75, 6004–6026.

Schmitt, A.D.S., Stille, P., 2005. The source of calcium in wet atmospheric deposits: Ca-Sr isotope evidence. Geochim. Cosmochem. Acta 69 (14), 3463–3468.

Schmitt, A.D., Chabaux, F., Stille, P., 2003. The calcium riverine and hydrothermal isotopic fluxes and the oceanic calcium mass balance. Earth Planet. Sci. Lett. 213 (3–4), 503–518.

Sequeira, R., Lai, C.C., 1998. An analysis of the representative composition of rainwater at six locations in Hong Kong. Water Air Soil Pollut. 107, 289–301.

Skulan, J., DePaolo, D.J., Owens, T.L., 1997. Biological control of calcium isotopic abundances in the global calcium cycle. Geochim. Cosmochim. Acta 61 (12), 2505–2510.

Stevenson, E.I., Aciego, S.M., Chutcharavan, P., Parkinson, I.J., Bruton, K.W., Blakowski, M.A., Arendt, C.A., 2016. Insights into combined radiogenic and stable strontium isotopes as tracers for weathering processes in subglacial environments. Chem. Geol. 429, 33–43.

Stevenson, R., Pearce, C.R., Rosa, E., Helie, J.-F., Hillaire-Marcel, C., 2018. Weathering processes, catchment geology and river management impacts on radiogenic (^{87}Sr/^{86}Sr) and stable ($\delta^{88/86}$Sr) strontium isotope compositions of Canadian boreal rivers. Chem. Geol. 486, 50–60.

Tu, J., Wang, H., Zhang, Z., Jin, X., Li, W., 2005. Trends in chemical composition of precipitation in Nanjing, China, during 1992-2003. Atmos. Res. 73, 283–298.

Wang, H., Han, G., 2011. Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China. Atmos. Res. 99, 190–196.

Wu, Q., Han, G., 2015. Sulfur isotope and chemical composition of the rainwater at the Three Gorges Reservoir. Atmos. Res. 155, 130–140.

Wu, Q., Han, G., Tao, F., Tang, Y., 2012. Chemical composition of rainwater in a karstic agricultural area, Southwest China: the impact of urbanization. Atmos. Res. 111, 71–78.

Xu, Z., Han, G., 2009. Chemical and strontium isotope characterization of rainwater in Beijing, China. Atmos. Environ. Times 43, 1954–1961.

Xu, Z., Li, Y., Tang, Y., Han, G., 2009. Chemical and strontium isotope characterization of rainwater at an urban site in Loess Plateau, Northwest China. Atmos. Res. 94, 481–490.

Zhao, Z., Tian, P., Fischer, E., Li, Z., Jiao, K., 2008. Study of chemical composition of precipitation at an alpine site and a rural site in the Urumqi River Valley, Eastern Tien Shan, China. Atmos. Environ. Times 42 (39), 8934–8942.

Zhao, D., Xiong, J., Xu, Y., Chan, W., 1988. Acid rain in southwestern China. Atmos. Environ. 22, 349–358.