



Strontium isotope and major ion chemistry of the rainwaters from Guiyang, Guizhou Province, China

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Abstract

Twenty-two rainwater samples from Guiyang city, southwestern China, have been analyzed for their chemical compositions and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, with a main purpose to get a better understanding of the general features of rainwater in Guiyang city and their correspondences to human activities. The rainwaters studied are almost acidic ($\text{pH}=4.53$) and show big changes in major ion composition. Ca^{2+} and Mg^{2+} are the principal cations in the rainwaters and their mean values are $56.6 \mu\text{mol/L}$ ($12.5\text{--}163.8 \mu\text{mol/L}$) and $12.8 \mu\text{mol/L}$ ($4.5\text{--}47.3 \mu\text{mol/L}$), respectively. The sum of Ca^{2+} and Mg^{2+} accounts for 78%–96% of the total cations in the studied rainwaters. Na^{+} was the least abundant of the major cations with a mean content of $4 \mu\text{mol/L}$ ($0.9\text{--}7.8 \mu\text{mol/L}$). SO_4^{2-} is the predominant anion, with a mean content of $94 \mu\text{mol/L}$ ($33.5\text{--}279.4 \mu\text{mol/L}$), coming next is NO_3^{-} with a mean content of $48 \mu\text{mol/L}$ ($2.1\text{--}251.8 \mu\text{mol/L}$). SO_4^{2-} and NO_3^{-} together account for 77%–99% of the total anions.

Ca^{2+} and Mg^{2+} in the rainwater are most likely from dissolution of carbonate minerals in dust or aerosol, unlike K^{+} that shows more contribution of anthropogenic sources to the rainwater. Na^{+} does not vary in concentration with Cl^{-} . Significant enrichment of Cl^{-} relative to Na^{+} as compared with sea water indicates negligible contribution of marine source, which is supported by the evidence that the total rainwater samples show lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (ranging from 0.707934 to 0.709080) than sea water. The rainwater samples are characterized by high contents of NO_3^{-} , SO_4^{2-} , and Cl^{-} relative to Na^{+} , as compared to the rainwater from other areas in the world, suggesting that the anions (NO_3^{-} , SO_4^{2-} , and Cl^{-}) have mainly of anthropogenic sources. Sr isotope shows potential to trace sources of contaminants when combined with other chemical factors: covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with $\text{Cl}^{-}/\text{Na}^{+}$ in the rainwater suggest presence of at least two anthropogenic sources for the rainwater samples studied. The coal-combustion industries are probably the major atmospheric contaminant sources in Guiyang city.

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1. Introduction

Land-use and industrial activities are considered the most important driving forces in the ongoing processes of atmospheric chemistry alteration. Most of these anthropogenic influences on the atmospheric chemistry are due to emissions of nitrogen and sulfur compounds. Therefore, the increasing worldwide industrialization has let the problem of acidic deposition receive more and more attention because of its notable direct adverse effects on ecosystem and indirect effects on human health (Lara et al., 2001; Hu et al., 2003).

With a fast economic development, energy consumption has increased significantly in the last two decades in Guizhou Province, China. This has given rise to widespread coal-fired power plants and heating systems built-up at an astonishing speed. Acid rain, therefore, has been a serious atmospheric environment problem especially for several big cities in Guizhou Province for many years. As early as late 1970s, acid rain has already been recognized as a potential environmental problem in southwestern China (Zhao and Seip, 1991; Zhao et al., 1988, 1994; Seip et al., 1995, 1999). However, studies on the chemistry and Sr isotopic composition of rainwater are few. Strontium isotope ratios in rainwater from several areas in the world have been reported by several authors (Graustein and Armstrong, 1983; Gosz and Moore, 1989; Aberg et al., 1989; Andersson et al., 1994; Dupre et al., 1994; Negrel and Roy, 1998). Strontium from different sources has a very distinct isotopic signature, and hence can be used to distinguish various aerosol sources (Herut et al., 1993; Aberg, 1995). Sr isotopes are expected to provide insights into the source of base cations in rainwater, particularly Ca, which is not well constrained from concentration data alone. In order to identify the contaminant sources and quantify their fluxes to the catchments, we have conducted a study on variations in chemical and Sr isotopic composition of the rainwater of Guiyang, a capital city of Guizhou Province.

2. Sampling site

Acid rain has been observed particularly in the middle northern part of the Guizhou Province. Guizhou

Province has a mountainous topography and cities there are often located in basins surrounded by high mountains. The soil is mainly acidic yellow earth and red earth, which cover 39% and 11% of the total area of the province, respectively. More than 70% of the whole area is composed of calcareous (Zhao and Seip, 1991). Guiyang (26.34 N, 106.43 E) is a capital city of Guizhou Province, with more than 1.34 million urban population. The city lies in a wide karst valley basin with an elevation of around 1000 m. The lithological characteristic of Guiyang city is dominated by sedimentary strata, most of which are carbonate and clastic rocks (Fig. 1).

The climate is sub-tropical and the average temperatures range from -1°C in the winter to 30°C in the summer. The dry season lasts from November to April and the wet season from May to October. Seventy-five percent of the total annual rainfall occurs in the wet season. Rainwater samples were collected on the roof of the building 28 in the Institute of Geochemistry, Chinese Academy of Sciences (CAS). Sampling was carried out at least 150 cm above the local roof level. This sampling site is located at the east-north part of Guiyang city and is at an elevation of 1080 m. No specific pollution sources or point sources are adjacent to the sampling site. Because the wind direction is usually east-north, the sampling site actually is located at the windward of the industrial districts of Guiyang city. It hence had avoided the direct industrial emission. Therefore, the sampling site has the atmosphere–environment characteristics of residential uptown.

3. Sampling and analytical procedures

The samplers were 2L polyethylene bottles, which were cleaned with acid (2–3 N HCl) and finally rinsed with Milli-Q water and dried. In order to minimize contributions from dry fallout, special attention was paid to opening the sampler as quickly as possible after the onset of rainfall. Since rainwater has very different pH value and chemical composition within first 20 min of each rain event (Dupre et al., 1994; Tuncel and Ungör, 1996), we collected bulk rainwater samples after ~30 min from start of each rain event. There were several months during which the sampling failed due to inadequate amount of precipitation.

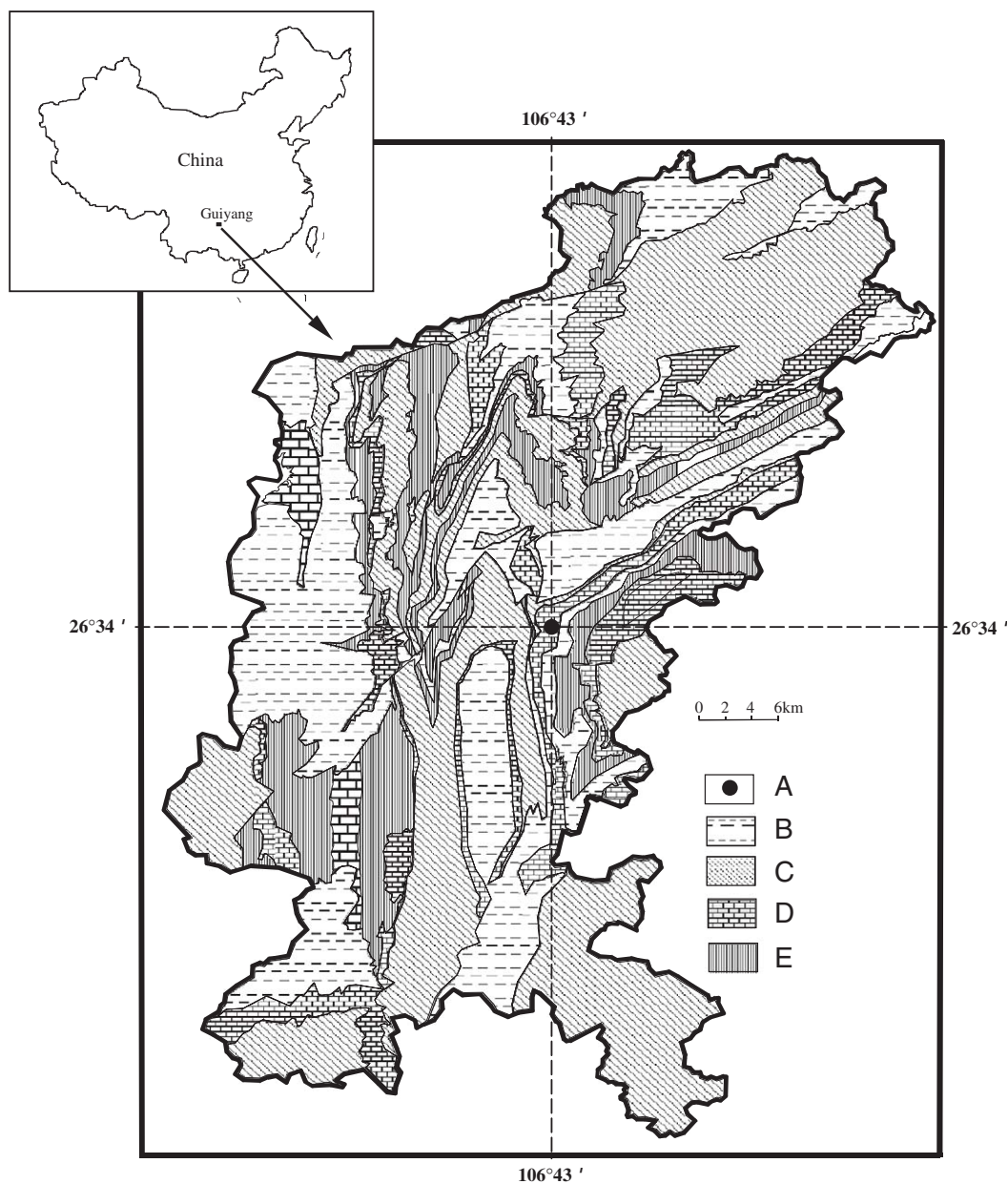


Fig. 1. A sketch map showing the lithology of Guiyang city, southwestern China. The legends: A stands for sample site, B for clastic sedimentary, C for dolomite, D for limestone, and E for carbonate rocks interbedded with clastic rocks (carbonate rocks account for 70%–90%).

Twenty-two rainwater samples were collected during the period from Jan. 11 in 1999 to Oct. 24 in 2001. Most of our samples were collected in the rainy season, from June to July.

pH and conductivity values were measured at sampling sites with a portable pH and salt conductivity

meter. HCO_3^- was titrated by HCl soon after collection. Immediately after collection, all the water samples were filtered through 0.22 μm membrane filters (Millipore) and a small portion of these samples was stored for measuring anions, while another portion was acidified with ultra-purified nitric acid to pH < 2

after collection for measuring cations and isotopic composition. All of the samples were stored at 4 °C for analysis. Major cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) were determined by Atomic Absorption Spectrometry (AAS). The concentrations of dissolved Sr^{2+} were measured by ICP-MS. Anions (Cl^- , SO_4^{2-} , NO_3^-) were measured by ionic chromatography. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by analysis of these quality control (QC) standards before, during and after the analysis of a set of samples. The analytical precision was better than $\pm 5\%$.

Separation of strontium from other major elements for isotopic analysis was carried out by a conventional ion-exchange technique using a Dowex 50 W-8X 200–400 mesh resin in HCl media. The isotopic compositions of Sr were determined on a VG354 mass spectrometer with five Faraday collectors in the Institute of Geology, CAS, Beijing. The value $^{87}Sr/^{86}Sr$ for the NBS987 strontium standard was 0.710238 ± 0.000021 (2δ , $n=25$) during the measurement period of these samples.

4. Results and discussions

4.1. Compositional variations of major ions

The concentration and isotope data of major ions and Sr are given in Table 1. The conductivity values of the rainwater samples vary from 19 to 92 $\mu S/cm$. No correlation between conductivity and the amount of the collected rainwater has been found. The pH values of rain samples range between 3.55 and 6.83, during which 19 rainwater samples have pH values smaller than 5.6. The mean value is 4.53. Rainwater with pH value below 5.6 is due to the presence of natural H_2SO_4 , weak organic acids, or anthropogenic emission of H_2SO_4 and/or HNO_3 . HCO_3^- is significantly present in the higher pH ranges of $pH > 5.5$, but can be neglected in the lower pH ranges of < 5.5 (Noguchi et al., 1995). The higher pH values reported here could be the result of dissolution of windblown dust with a high $CaCO_3$ content, so the high pH value does not correspond with the high HCO_3^- concentration. Even $pH > 5.5$, we still couldn't measure the concentration of HCO_3^- .

Table 1
Concentrations ($\mu mol/L$) of major ions and Sr isotope ratios in rainwater from Guiyang city, southwestern China

Sample	Date (y-m-d)	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	K^+	Na^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	$^{87}Sr/^{86}Sr$
Y1	99-01-11	4.59	u.d.	6.77	8.23	33.5	2.82	1.74	18.8	8.23	0.0913	0.708224
Y2	99-06-09	6.83	0.008	28.6	28.5	106.9	24.9	4.35	97.5	8.23	0.0663	0.708221
Y3	99-06-17	4.86	0.020	7.50	29.0	60.7	10.0	7.39	38.8	10.3	0.0726	0.708025
Y4	99-06-21	4.09	0.010	128.1	184.1	127.1	9.49	5.65	38.8	12.4	0.0516	0.708450
Y5	99-06-22	3.78	0.014	2.68	21.5	111.6	5.64	4.78	50.0	16.5	0.0813	0.708069
Y6	99-06-24	3.61	u.d.	121.2	110.7	279.4	9.74	5.22	141.3	47.3	0.209	0.708023
Y7	99-06-26	4.61	0.099	17.5	31.0	123.9	9.74	5.65	78.8	16.5	0.217	0.708350
Y8	99-06-29	4.87	u.d.	5.16	16.6	49.2	5.64	3.04	33.8	6.17	0.0530	0.708331
Y9	99-06-30	4.33	u.d.	8.35	16.6	62.3	4.62	3.48	55.0	14.4	0.0251	0.708320
Y10	99-07-01	3.98	0.002	9.59	20.7	56.6	3.85	0.87	21.3	12.4	0.0249	0.708473
Y11	99-07-07	4.48	u.d.	9.17	42.2	69.7	6.41	2.17	32.0	4.53	0.0527	0.708096
Y12	99-07-15	3.64	u.d.	0.85	1.29	43.9	1.54	0.87	32.5	6.17	0.0211	0.708121
Y13	99-10-31	4.54	0.060	23.2	101.7	112.4	26.7	6.09	56.8	12.4	0.0956	0.707934
Y14	99-12-21	5.71	0.022	47.0	96.6	188.4	44.1	7.83	163.8	37.0	0.328	0.709080
Y15	2000-06-19	4.86	u.d.	4.23	2.06	36.1	2.31	0.87	25.0	10.3	0.205	0.708236
Y16	2000-06-20	4.76	u.d.	5.92	2.06	59.9	2.31	0.87	21.0	7.00	0.183	0.708184
Y17	2000-07-20	4.56	0.004	4.17	20.7	107.5	6.15	3.48	95.3	9.05	0.171	0.708092
Y18	2000-08-26	4.35	0.004	2.00	22.3	98.4	13.3	4.78	57.0	11.1	0.0913	0.707983
Y19	2001-04-19	6.24	0.010	6.94	29.8	128.6	21.8	6.52	118.0	10.7	0.203	0.708262
Y20	2001-07-03	3.86	u.d.	13.9	251.8	52.2	3.85	6.09	12.5	4.94	0.0150	0.708025
Y21	2001-07-07	3.66	0.003	8.74	16.9	69.6	15.6	2.61	33.8	10.7	0.0243	0.708162
Y22	2001-10-24	3.55	u.d.	4.15	7.19	90.3	11.8	2.61	23.5	4.53	0.0389	0.708160
Average		4.53		21.17	48.24	94.00	11.01	3.95	56.58	12.76	0.11	0.708219

u.d. stands for under detection limit.

Seven major ions in the rainwater samples were measured. Since the NH_4^+ has not been determined, it is impossible to assess electro-neutrality because the NH_4^+ is commonly one of the major ions in rainwater (Sanusi et al., 1996; Noguchi et al., 1995). Compared to the cations, the anions show big variation in concentration, changing with more than two orders. Fig. 2 shows the variations of major ion compositions. The corresponding data of the rainwaters from several areas in the world are also shown in the figure for comparison, since our sampling procedure is similar to those used in the studies. From Fig. 2, it is clear that the rainwaters of Guiyang city have more Ca^{2+} , Mg^{2+} , SO_4^{2-} and NO_3^- , with less K^+ , Na^+ , and Cl^- , in comparison with the referenced rainwaters. Ca^{2+} and Mg^{2+} are the most abundant cations with a mean weighted concentration of 56.6 and 12.8 $\mu\text{mol/L}$, respectively. The contents of Ca^{2+} vary from 12.5 to 163.8 $\mu\text{mol/L}$ and Mg^{2+} from 4.5 to 47.3 $\mu\text{mol/L}$. The sum of Ca^{2+} and Mg^{2+} accounts for 78%–96% of the total cations in the rainwater samples. Sodium was the least abundant major cation with a mean weighted content of 4 $\mu\text{mol/L}$, ranging from 0.9 to 7.8 $\mu\text{mol/L}$.

As it can be seen from Fig. 2b, SO_4^{2-} was the most abundant anions, and its concentrations range from 33.5 to 279.4 $\mu\text{mol/L}$, with a mean weighted concentration of 94 $\mu\text{mol/L}$. SO_4^{2-} accounts for 28%–94% of the total anions. The second abundant anion is NO_3^- , with variation range from 2.1–251.8 $\mu\text{mol/L}$, and a mean concentration of 48 $\mu\text{mol/L}$. SO_4^{2-} and NO_3^-

Table 2

Matrix of correlation coefficients of ionic concentrations ($\mu\text{mol/L}$) in rainwater sample from Guiyang

Ions	$[\text{H}^+]$	$[\text{K}^+]$	$[\text{Na}^+]$	$[\text{Ca}^{2+}]$	$[\text{Mg}^{2+}]$	$[\text{Cl}^-]$	$[\text{NO}_3^-]$	$[\text{SO}_4^{2-}]$
$[\text{H}^+]$	1							
$[\text{K}^+]$	-0.25	1						
$[\text{Na}^+]$	-0.23	0.63	1					
$[\text{Ca}^{2+}]$	-0.18	0.70	0.59	1				
$[\text{Mg}^{2+}]$	0.15	0.42	0.43	0.76	1			
$[\text{Cl}^-]$	0.18	0.21	0.37	0.41	0.64	1		
$[\text{NO}_3^-]$	0.09	0.18	0.55	0.11	0.24	0.60	1	
$[\text{SO}_4^{2-}]$	0.17	0.52	0.56	0.84	0.87	0.72	0.33	1

together account for 77%–99% of the total anions measured.

4.2. Correlation factors

Relationships between measured components were examined through the analysis of linear correlation, and the correlation matrix for all samples is given in Table 2. The sulfate shows good correlations with Ca^{2+} and Mg^{2+} , with correlation coefficients of 0.84 and 0.87, respectively. This indicates that calcium (and/or magnesium) sulfate is the important compound in precipitation. Sulfate shows good correlation with Cl^- ($r=0.72$), but not with NO_3^- ($r=0.33$), which is not the case expected because nitrate and sulfate as both are photochemically produced and hence should have good correlation. Among the cations, there are good correlations between Mg^{2+}

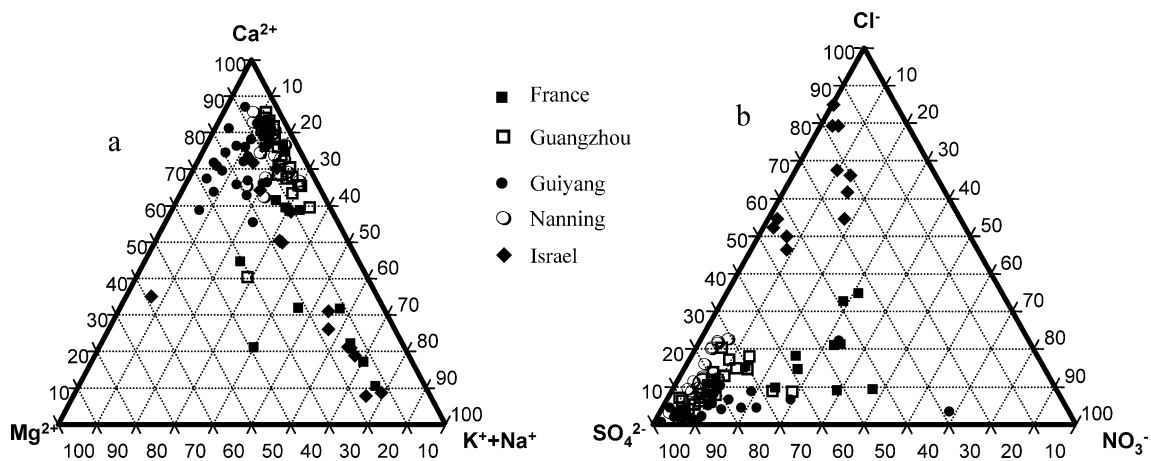


Fig. 2. Ternary diagrams showing cation (diagram a) and anion compositions (diagram b). The data of rainwaters collected at other areas in China and the world are also shown here for comparison. Data sources are Herut et al. (1993) for Israel rainwater, Negrel and Roy (1998) for France rainwater, Qi and Wang (1995) for Nanning and Guangzhou rainwater.

and Ca^{2+} ($r=0.76$), Ca^{2+} and K^+ ($r=0.70$), as well as Na^+ and K^+ ($r=0.63$).

4.3. Origins of major ions in the rainwater

There are, in general, three main sources for the dissolved solids in rainwater, which are from sea salt aerosols, from terrestrial aerosols (soil dust, biological emissions) and from human sources, such as industrial and agricultural activities, burning of vege-

tation and fossil fuel (Negrel and Roy, 1998). The rainwater affected by human activities is usually rich in Ca^{2+} , and that affected by sea spray in Na^+ . The rainwater with high contents of both Ca^{2+} and Mg^{2+} is most likely affected by dissolution of mineral dust. For the anions of marine source will be characterized by enrichment in Cl^- and relative depletion in SO_4^{2-} and NO_3^- , and hence the data points should fall close to the apex of the Cl^- , as shown in Fig. 2b. On the other hand, if coming from human activities, SO_4^{2-} or

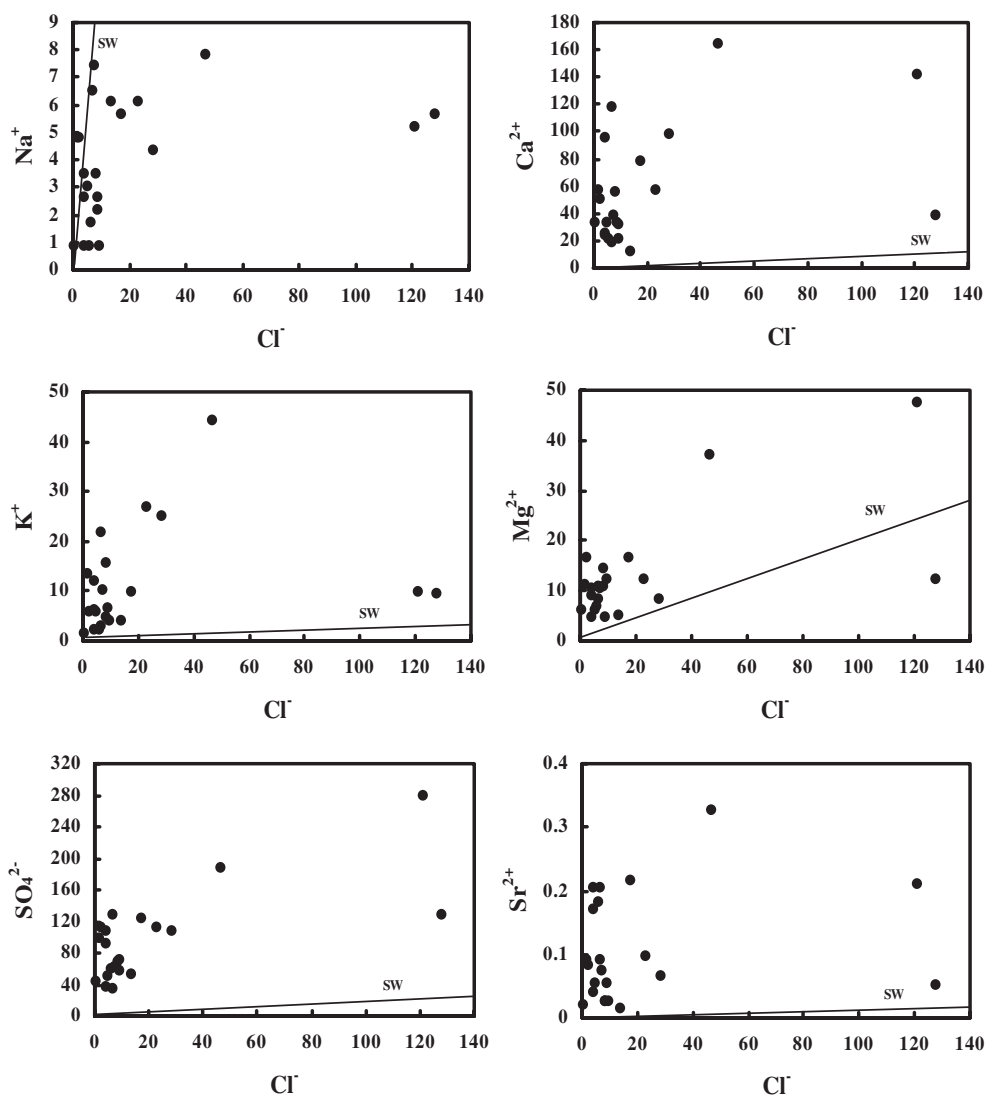


Fig. 3. The relationship between solutes and chloride in the rainwater samples. The line in each diagram shows the corresponding ratios of sea water (sea water data from Berner and Berner, 1986).

NO_3^- will have high content, and hence the data points should fall close to the SO_4^{2-} – NO_3^- line in the anion ternary diagram. In the following, we will discuss the origins of major anions and cations based on the variations in chemical composition of the rainwaters.

4.3.1. Origins of the anions

Fig. 3 shows the correlations of Cl^- with other cations and SO_4^{2-} . As compared with sea water, the rainwaters collected at Guiyang city pose significantly lower Cl^- relative to other ions except for Na^+ , with most Cl^-/Na^+ equivalent ratios larger than that ($\text{Cl}^-/\text{Na}^+=1.17$) of seawater (Fig. 4). This suggests that the high content of Cl^- relative to sea water is mainly contributed by anthropogenic sources, far from a marine origin. Only two rain events are of lower Cl^-/Na^+ ratios, which can be explained by the presence of terrigenous Na^+ , or in terms of replacement of Cl^- by SO_4^{2-} or NO_3^- (Keene et al., 1990; Clegg and Brimblecombe, 1985, 1986). In fact, both mechanisms for producing low Cl^-/Na^+ ratio are possible, since the rainwaters from Guiyang have high NO_3^- and SO_4^{2-} concentrations, and the Na^+ in crustal aerosol could be easily washed out.

Fig. 5 shows the covariations of Na^+ -normalized K^+ , SO_4^{2-} and NO_3^- values. The rainwater samples from Guiyang have higher contents of K^+ , SO_4^{2-} , NO_3^- relative to Na^+ , when compared with the rainwaters from Israel and France, and even with those from

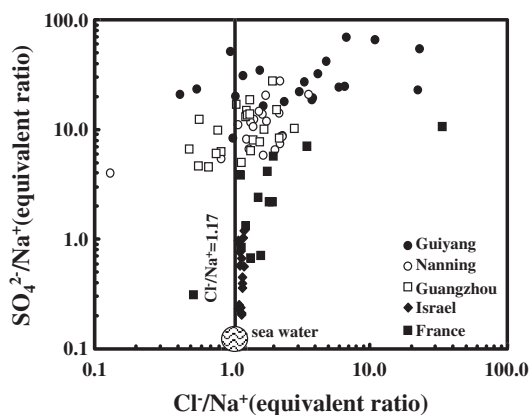


Fig. 4. Covariation of $\text{SO}_4^{2-}/\text{Na}^+$ with Cl^-/Na^+ ratios in the rainwater samples collected at Guiyang, and from other areas in China, France and Israel (data sources and symbols are the same as those in Fig. 2).

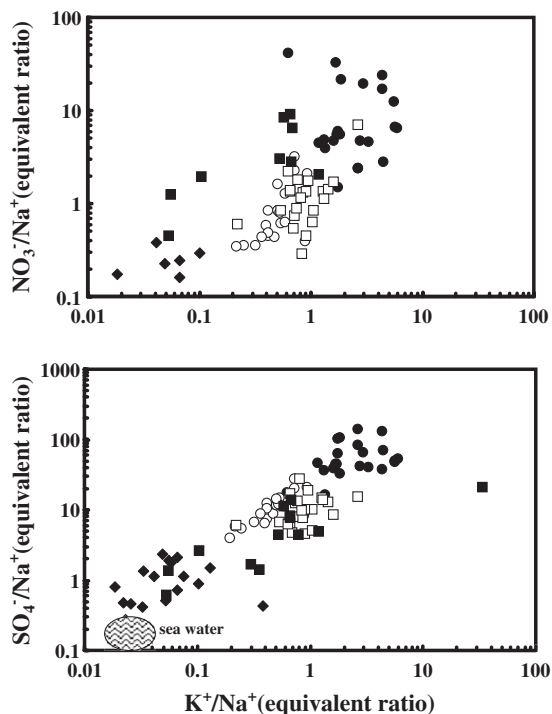


Fig. 5. Covariation of $\text{SO}_4^{2-}/\text{Na}^+$ and $\text{NO}_3^-/\text{Na}^+$ with K^+/Na^+ ratios in the rainwaters from Guiyang and other areas (data sources and symbols are the same as those in Fig. 2).

Guangzhou and Nanning cities (Fig. 5). The enrichment of SO_4^{2-} and NO_3^- relative to Na^+ in the rainwaters from Guiyang can be attributed to inputs of gaseous sulfuric and nitric acids as well as inputs due to the collection of sulphate- and nitrate-containing aerosols. Guizhou Province is rich in coal resources and still has many coal-combustion power plants located around big cities. According to the chemical composition of the rainwaters studied, the coal-combustion industries in or around big cities in Guizhou Province still show large impact on the atmospheric environment.

4.3.2. Origins of the cations

Na^+ and Cl^- in rain are generally assumed to have their origin of seawater, while Ca^{2+} , particularly in inland rain, is held to be largely terrestrial. Identifying the provenance of Ca^{2+} in rainwater has a special importance to the study of acid rain problems, because this element is dominant cation that neutralizes acid and is indispensable for plant growth. There are three main origins for the Ca^{2+} in rainwater. The first source

is that Ca^{2+} may be of anthropogenic origin. For example, it may be emitted by human activities such as traffic, cement work, etc. The second possibility is of carbonate weathering. Guiyang city is located in the center of a karstic basin composed mainly of limestone, where soil contains high concentration of Ca^{2+} . The third possible origin for Ca^{2+} is the long-range transport of soil dust. Since Guiyang city is located in basins surrounded by high mountains, we think that the first two origins probably explain the high level of Ca^{2+} contents in the precipitations collected at Guiyang.

The correlation factor analysis indicates that Mg^{2+} has good correlation with Ca^{2+} ($r=0.78$), so the Mg^{2+} should have a common source with Ca^{2+} . Na^+ does not vary in association with Cl^- in these samples, suggesting their different origins. However, Na^+ has slightly good correlation with Ca^{2+} and Mg^{2+} . From Fig. 5, it can be seen that the rainwaters collected at Guiyang city shows the highest K^+/Na^+ ratios. The high K^+/Na^+ ratio probably suggests an anthropogenic origin for K^+ , since it increases with increasing $\text{SO}_4^{2-}/\text{Na}^+$ and $\text{NO}_3^-/\text{Na}^+$ ratio for the rainwaters studied by previous authors.

4.4. Sr and its isotope ratios

It has well been documented by studies that the rainwater in the world shows various Sr isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$) from 0.7079 to 0.7200 (Graustein and Armstrong, 1983; Gosz and Moore, 1989; Aberg et al., 1989; Andersson et al., 1994; Dupre et al., 1994; Herut et al., 1993). The Sr in the rainwaters from Guiyang has concentration varying from 0.02 to 0.33 $\mu\text{mol/L}$ and isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) from 0.707934 to 0.709080. All of the samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than the ratio ($^{87}\text{Sr}/^{86}\text{Sr}=0.70917$) of present-day sea water (Dia et al., 1992), which argues clearly against a main marine origin for Sr. No simple binary mixing correlations has been found between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\text{Mg}^{2+}/\text{Sr}^{2+}$, $\text{Na}^+/\text{Sr}^{2+}$, $\text{K}^+/\text{Sr}^{2+}$, $\text{Ca}^{2+}/\text{Sr}^{2+}$ ratios (Fig. 6). Accordingly, more than two sources should be responsible for the variation of the Sr isotope and the related element ratios. If Sr has sources of calcite and dolomite dissolution, its isotope ratio will be most likely during a range of 0.7075 to 0.7080, and of 0.7080 to 0.7100, respectively (Han and Liu, 2004), while Sr from

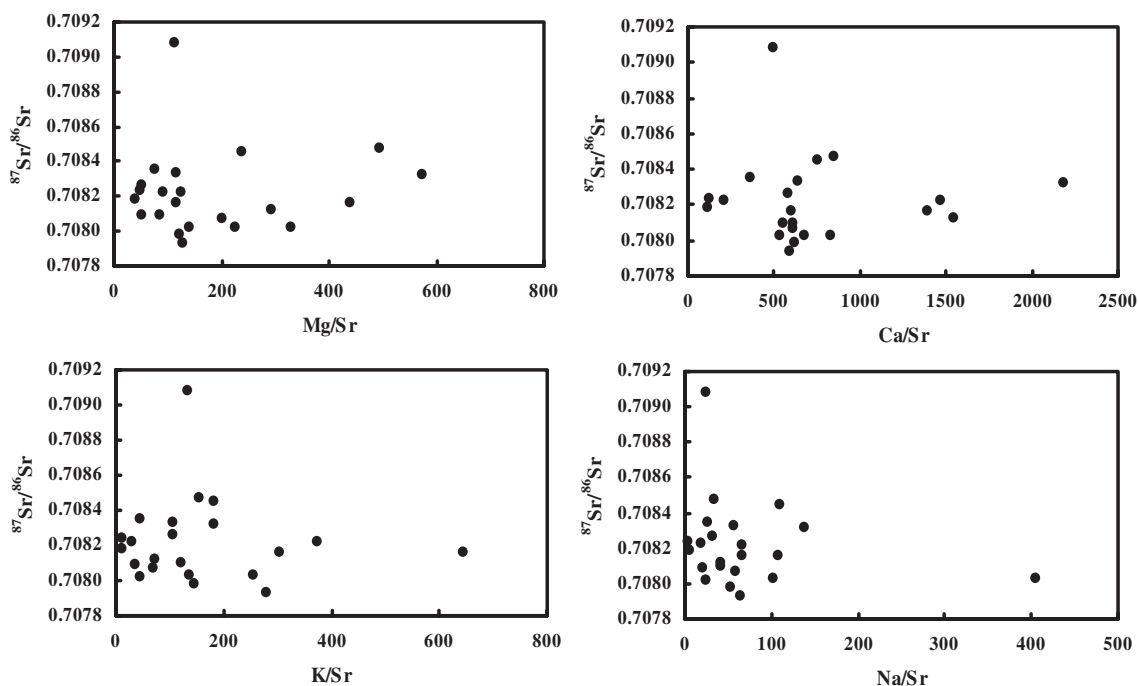


Fig. 6. Correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ and chemical elements ratios ($\text{Ca}^{2+}/\text{Sr}^{2+}$, $\text{Mg}^{2+}/\text{Sr}^{2+}$, $\text{K}^+/\text{Sr}^{2+}$ and $\text{Na}^+/\text{Sr}^{2+}$) in the rainwaters from Guiyang, southwestern China.

weathering of silicate minerals be characterized high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, generally larger than 0.7150. No data exist on Sr concentrations or isotopic compositions of other possible pollutants (automobile exhaust, coal combustion, incinerators) except the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of fertilizers that ranges from 0.7079 and 0.7087 (Negrel and Deschamps, 1996). Since the Sr isotope ratios of typical contaminant sources for the rainwaters collected at Guiyang have not been characterized, it is difficult to identify the sources for Sr based on its ratio only.

In Fig. 7 shown is the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ with Cl^-/Na^+ ratios in the rainwaters from Guiyang city. Cl^-/Na^+ ratio can be used as indicator of sources: marine source has Cl^-/Na^+ ratio of 1.17 and anthropogenic sources should have higher ratios. As seen from Fig. 7, although a general positive relationship exists between $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl^-/Na^+ ratio, at least three source mixing is necessary to interpret the data distribution. We have estimated the $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl^-/Na^+ ratios, together with the Sr and Na concentrations for the three end-member rainwaters arbitrarily according to the rainwater samples Y18, Y4 and Y14 (the estimated values for each end-member are given in the figure). The first source is probably from calcite mineral dissolution, possessing the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl^-/Na^+ ratio as well as the lowest Na^+ . In contrast, other two end-members are characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl^-/Na^+ ratio and high Na content, in accordance with signatures of anthropogenic sources due to their high Cl^-/Na^+ ratio. The

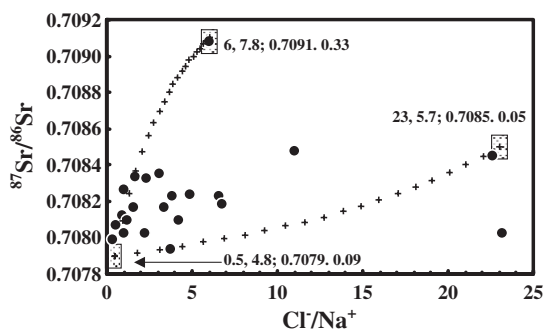


Fig. 7. Variation of Sr isotope ratios with Cl^-/Na^+ molar ratios in the rainwater samples. The binary mixing lines were calculated based on the isotope and element ratios estimated for each end-members (see the text for detail). The estimated characteristic values of Cl^-/Na^+ , Na^+ (in $\mu\text{mol/L}$), $^{87}\text{Sr}/^{86}\text{Sr}$, Sr ($\mu\text{mol/L}$) for each end-member are also shown in the figure.

mixing lines between calcite source end-member and two anthropogenic sources have calculated, on which one mark (cross) stands for increase of 5% of one end-member. Based on the estimation, it is clear that most rainwaters have cations mainly originated from dissolution of crustal minerals: however, the influence of high-Cl anthropogenic source on the rainwaters in terms of chemical and Sr isotopic composition is large.

5. Conclusions

The rainwaters collected mainly in summer season during two years from Guiyang city, southwestern China, has low pH values, averaging on $\text{pH}=4.53$. The chemistry of the rainwater shows the dominance of Ca^{2+} , Mg^{2+} , NO_3^- and SO_4^{2-} , and big changes in major ion composition, largely different from those of the rainwater from several cities in China and the world. Variations in chemical composition show multi-component origins of major ions in the rainwater. The rainwater is characterized by high contents of NO_3^- , SO_4^{2-} , and Cl^- relative to Na^+ , as compared to the rainwater from other areas in the world, from which we consider that the anions (NO_3^- , SO_4^{2-} , and Cl^-) have mainly anthropogenic sources and that the coal-combustion industries are one main type of major atmospheric contaminant sources in Guiyang city.

Ca^{2+} and Mg^{2+} in the rainwater are most likely from dissolution of carbonate minerals in dust or aerosol, unlike K^+ that shows more contribution of anthropogenic sources to the rainwater. Na^+ does not vary in concentration with Cl^- . Significant enrichment of Cl^- relative to Na^+ as compared with sea water indicates negligible contribution of marine source.

The Sr concentrations vary from 0.02 to 0.33 $\mu\text{mol/L}$, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary during a small range (0.707934–0.709080) in the rainwater in Guiyang. All of the samples have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than that of present-day sea water. Together with the compositional variations of major ions, this argues strongly against a marine origin for the major solutes in the rainwater. Covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with Cl^-/Na^+ in the rainwater suggests presence of at least two anthropogenic sources, and importance of carbonate mineral dissolution for source of Sr^{2+} and also probable Ca^{2+} and Mg^{2+} . Although it is difficult to identify

the sources of Sr and other cations in rainwater, only based on Sr isotope ratio because of variable ratios of contaminants, Sr isotope shows potential to trace sources of contaminants when combined with other chemical factors.

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