

Chemical and strontium isotope characterization of rainwater in Beijing, China

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ABSTRACT

Major ion concentrations and Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured in rainwater samples collected at an urban site in Beijing over a period of one year. The pH value and major ion concentrations of samples varied considerably, and about 50% of the rainwater studied here were acidic rain with pH values less than 5.0. Ca^{2+} and NH_4^+ were the dominant cations in rainwaters and their volume weighted mean (VWM) values were $608 \mu\text{eq l}^{-1}$ (14–1781 $\mu\text{eq l}^{-1}$) and $186 \mu\text{eq l}^{-1}$ (48–672 $\mu\text{eq l}^{-1}$), respectively. SO_4^{2-} was the predominant anion with VWM value of $316 \mu\text{eq l}^{-1}$ (65–987 $\mu\text{eq l}^{-1}$), next was NO_3^- with VWM value of $109 \mu\text{eq l}^{-1}$ (30–382 $\mu\text{eq l}^{-1}$).

Using Na as an indicator of marine origin, and Al for the terrestrial inputs, the proportions of sea salt and terrestrial elements were estimated from elemental ratios. More than 99% of Ca^{2+} and 98% of SO_4^{2-} in rainwater samples are non-sea-salt origin. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were used to characterize the different sources based on the data sets of this study and those from literatures. Such sources include sea salts ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.90917$), soluble soil dust minerals originating from either local or the desert and loess areas (~ 0.7111), and anthropogenic sources (fertilizers, coal combustion and automobile exhausts). The high concentrations of alkaline ions (mainly Ca^{2+}) in Beijing atmosphere have played an important role to neutralize the acidity of rainwater. However, it is worth noting that there is a remarkable acidification trend of rainwater in Beijing recent years.

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1. Introduction

Rapid economic growth and increased energy demand have resulted in severe air pollution problems throughout China, particularly in, and near the large cities (Larssen and Carmichael, 2000). Emissions of SO_2 associated with coal combustion have considerably increased in China since the late 1970s, leading to significant deposition of acid rain (Zhao et al., 1988). In China, the estimated emissions of SO_2 to the atmosphere were about 22 million metric tons in 2003 (Larssen et al., 2006). Since coal combustion is a major source of air pollution in China, the major components of common air pollutions are particulates and SO_2 , which up to now has been the most important precursor of acid rain in China. During the last three decades, the chemistry of precipitation has been widely investigated in many areas in China, such as southern, southwestern and eastern China, which are significantly affected by acid rain. Most studies on acid rain in China have focused on the distribution of precipitation pH and sulfur deposition (Zhao et al., 1988; Wang and Wang, 1995; Yu

et al., 1998; Larssen and Carmichael, 2000; Larssen et al., 2006; Aas et al., 2007; Huang et al., 2008). Fewer results have been published regarding the large cities in northern China. Moreover, there are obviously many sources of the dissolved species in rainwater. It is difficult to unravel the different sources, unless isotopes are used (Anderson et al., 1990). Sr isotopes are expected to provide insights into the source of base cations in rainwater. However, only a few data are available on $^{87}\text{Sr}/^{86}\text{Sr}$ in precipitation, which may result in a limitation to the use of Sr isotopes in atmospheric geochemistry (Nakano and Tanaka, 1997).

As a capital city for more than 850 years, there are numerous centuries-old buildings, monuments, ancient corroded copper and iron sculptures in Beijing. Acid rain will seriously damage and corrode these precious historical and cultural heritages. This study would present, for the first time, the results of Sr isotope ratios in rainwater collected over one-year period at an urban site in Beijing city. The purpose of this paper is to present and discuss the chemical characterization and Sr isotope signature in the rainwater, to gain an primary understanding of the rainwater chemistry, to identify possible sources that contribute to its chemical composition, and finally to deduce the causes of rain acidification tendency in Beijing.

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2. Sampling site

Beijing is located in the northern part of the North China Plain and geomorphologically it is high to the northwest and is low to the southeast, not far from the western slopes of the Yanshan Mountains, and about 150 km to the Bohai Sea. With a typical continental monsoon climate of northern temperate zone, there are four distinct seasons in Beijing. The average annual temperature is around 12 °C and the average annual precipitation is 626 mm.

Beijing is one of the most crowded cities in the world. According to China Daily's report, the population of the city has exceeded 17 million for the first time by the end of 2007. As the capital city of China, Beijing is the nation's political, economic and cultural center as well as Chinese most important center for international contacts. A modern urban road network has been completed and it is backboneed by urban expressways and five ring roads. The average density of road network is about 0.92 km/km² and it reaches about 2.62 km/km² within the 5th ring road. For years, the government has promoted the auto industry, and China has been the world's second-largest vehicle market by unit sales, next to the United States. The amount of private car has exceeded 3.2 million in Beijing by the end of 2007.

3. Sampling and analytical procedure

The sampling site is located at the central part (N 39°56.549'; E 116°23.816') of Beijing city, and is at an elevation of 42 m (Fig. 1). The sampler was placed on the roof of a building about 10 m high from ground level in a residential area. The rainwater samples were collected manually from the beginning of each rain event with a funnel sampler that was located approximately 120 cm above the roof. Prior to use, the sampler was cleaned with acid (2–3 N HCl), rinsed with Milli-Q water (18.2 MΩ cm) and then dried. In order to prevent contaminations from dry deposition, special attention was paid to open the sampler as quickly as possible after the onset of

rainfall. Sixteen rainwater samples were collected from Jan. to Dec. in 2006. Most of our samples were collected in the rainy season, from July to August and there are no samples after September due to inadequate amount of precipitation.

The pH and conductivity values were measured instantaneously at the end of the rain events at sampling sites with a portable pH and salt conductivity meter. The rainwater samples were filtered through 0.22 μm Millipore membrane filters using a pre-cleaned Nalgene filter apparatus and the filtrate was separated into two aliquots. One was stored in unacidified polyethylene bottles for measuring anions and the other was acidified with ultra-purified nitric acid to pH <2 and stored in pre-cleaned polyethylene bottles for measuring cations, Sr concentrations and Sr isotopic ratios. Major anions (Cl⁻, SO₄²⁻, NO₃⁻) were measured by using an ionic chromatography (Dionex DX-120). NH₄⁺ concentrations were determined by spectrophotometry using the Nessler method. Major cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) were determined by ICP-AES (Thermo's IRIS Intrepid II). The concentrations of Sr²⁺ were measured by ICP-MS (VG POEMS III) in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures and the analytical precision is better than ±5%.

For determination of the ⁸⁷Sr/⁸⁶Sr isotopic ratio, all samples were analyzed by MC-ICP-MS (Finnigan Neptune) in the State Key Laboratory of Lithospheric Evolution, the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. Natural waters with low Sr concentration were preconcentrated by partial evaporation in a clean laboratory. Strontium was purified by standard cation-exchange procedure. Rb and Sr were first separated from the samples on a cation-exchange column loaded with Dowex 50 W-X8 200–400 mesh resin by elution of 2.0 M HCl. Following chemistry, all samples were taken up in 2% HNO₃ and introduced into the MC-ICP-MS. In most cases, this technique would result in Sr fractions with only small Rb interferences. The blank of this procedure is less than 100 pg of Sr. The measurement of Sr isotopes using mass spectrometer with an argon ICP source, such as Neptune, may induce an erroneous result due to Kr contamination of the argon gas. The measured ⁸⁶Sr ion beam was corrected for isobaric interferences from ⁸⁶Kr. For this, the ion beam of ⁸³Kr was monitored and the ⁸⁶Kr contribution to measured intensity at mass 86 was corrected for by using the ⁸⁶Kr/⁸³Kr ratio of 1.52 (Ehrlich et al., 2001; Waight et al., 2002). The reproducibility was verified by periodic determinations of the NBS 987 strontium standard. The average ⁸⁷Sr/⁸⁶Sr ratio of this standard for 25 determinations was 0.710235 ± 0.000022 (2σ, n = 25) during the course of the study.

4. Results and discussion

4.1. Ionic composition and pH value

The field data, major ions, strontium concentrations and ⁸⁷Sr/⁸⁶Sr isotopic ratios are given in Table 1. Statistics of the composition of major ions and pH values are presented in Table 2. The anion deficit (Σ⁻) – (Σ⁺) for rainwaters is –331.4 μeq l⁻¹. This imbalance is usually attributed to unmeasured anionic species, such as bicarbonate, acetate, formate, etc. (Losno et al., 1991; Negrel and Roy, 1998; Mouli et al., 2005). The values of arithmetic mean are higher than those of median, indicating that the frequency distributions are asymmetric and skewed by those high concentration values. The volume-weighted means (VWMS) are smaller than arithmetic means and medians, indicating that the higher concentrations are usually associated with lower precipitations. However, calcium ion

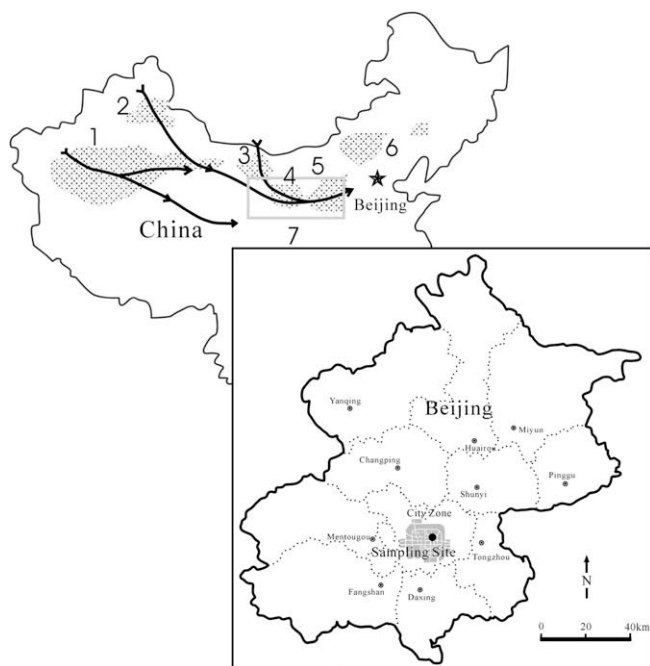


Fig. 1. Sketch map showing the sampling location and the desert areas around Beijing. 1. Taklamakan Desert; 2. Gurbantonggut Desert; 3. Badain Jaran Desert; 4. Tengli Desert; 5. Muus Desert; 6. Hunshandake Desert; 7. Loess Region. The forward trajectories indicate the sources of soil dust and the routes of its transportation.

Table 1
Concentration of major ions (in $\mu\text{eq l}^{-1}$), Al and Sr (in $\mu\text{mol l}^{-1}$), and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in rainwaters from Beijing city.

| Sample number | Date m-d-yr | pH | EC μScm^{-1} | F ⁻ $\mu\text{eq l}^{-1}$ | Cl ⁻ $\mu\text{eq l}^{-1}$ | NO ₃ ⁻ $\mu\text{eq l}^{-1}$ | SO ₄ ²⁻ $\mu\text{eq l}^{-1}$ | NH ₄ ⁺ $\mu\text{eq l}^{-1}$ | K ⁺ $\mu\text{eq l}^{-1}$ | Na ⁺ $\mu\text{eq l}^{-1}$ | Ca ²⁺ $\mu\text{eq l}^{-1}$ | Mg ²⁺ $\mu\text{eq l}^{-1}$ | Al ³⁺ $\mu\text{mol l}^{-1}$ | Sr ²⁺ $\mu\text{mol l}^{-1}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ | 2 σ |
|---------------|----------------|------|----------------------------|---|--|---|--|---|---|--|---|---|--|--|---------------------------------|------------|
| BJ-Snow-1 | 1-12-2006 | 4.63 | 138 | 30.47 | 216.36 | 374.03 | 484.73 | 203.56 | 34.17 | 179.93 | 717.29 | 146.04 | 29.39 | 0.463 | 0.709793 | 0.000020 |
| BJ-Snow-2 | 2-06-2006 | 5.53 | 29 | 17.47 | 126.01 | 83.15 | 94.29 | 47.77 | 10.07 | 32.46 | 153.38 | 32.82 | 3.95 | 0.121 | 0.709468 | 0.000016 |
| BJ-Rain-3 | 5-25-2006 | 5.28 | 74 | 19.58 | 105.16 | 151.74 | 339.88 | 175.00 | 29.35 | 18.88 | 234.05 | 61.14 | 7.16 | 0.085 | 0.709932 | 0.000022 |
| BJ-Rain-4 | 5-26-2006 | 4.36 | 40 | 7.16 | 98.87 | 74.21 | 180.88 | 129.56 | 12.83 | 11.35 | 26.01 | 4.99 | 1.97 | 0.009 | 0.709245 | 0.000032 |
| BJ-Rain-5 | 6-13-2006 | 4.77 | 83 | 9.89 | 114.81 | 93.56 | 373.29 | 180.19 | 49.61 | 37.39 | 276.27 | 48.92 | 6.51 | 0.132 | 0.710357 | 0.000020 |
| BJ-Rain-6 | 6-24-2006 | 6.73 | 69 | 16.32 | 108.55 | 107.68 | 309.02 | 268.47 | 26.33 | 25.41 | 172.38 | 51.40 | 0.40 | 0.066 | 0.710008 | 0.000021 |
| BJ-Rain-7 | 6-28-2006 | 5.69 | 81 | 16.05 | 122.74 | 136.94 | 400.60 | 293.14 | 18.61 | 45.27 | 131.50 | 42.98 | 1.73 | 0.071 | 0.709689 | 0.000018 |
| BJ-Rain-8 | 6-30-2006 | 6.68 | 114 | 34.42 | 126.83 | 222.44 | 503.48 | 328.19 | 42.52 | 22.67 | 491.13 | 92.16 | 0.65 | 0.164 | 0.709684 | 0.000016 |
| BJ-Rain-9 | 7-09-2006 | 4.45 | 13 | 6.79 | 84.99 | 30.31 | 64.81 | 64.65 | 3.83 | 3.78 | 14.49 | 2.14 | 0.34 | 0.0051 | 0.709118 | 0.000021 |
| BJ-Rain-10 | 7-10-2006 | 4.02 | 88 | 16.05 | 107.28 | 118.45 | 360.29 | 233.42 | 13.87 | 13.06 | 62.49 | 10.49 | 4.66 | 0.031 | 0.709760 | 0.000030 |
| BJ-Rain-11 | 7-12-2006 | 4.12 | 96 | 15.32 | 98.93 | 129.45 | 417.94 | 241.21 | 16.15 | 25.38 | 827.02 | 34.60 | 0.13 | 0.120 | 0.709357 | 0.000011 |
| BJ-Rain-12 | 7-13-2006 | 5.47 | 75 | 18.00 | 106.35 | 110.29 | 313.60 | 172.40 | 12.13 | 27.12 | 705.99 | 66.34 | 2.84 | 0.222 | 0.709540 | 0.000016 |
| BJ-Rain-13 | 8-08-2006 | 7.62 | 254 | 38.05 | 147.02 | 381.52 | 986.75 | 672.21 | 33.00 | 59.83 | 1781.2 | 115.71 | 0.88 | 0.297 | 0.709452 | 0.000012 |
| BJ-Rain-14 | 8-10-2006 | 4.54 | 82 | 19.37 | 107.79 | 133.63 | 413.29 | 299.63 | 16.91 | 20.17 | 1027.9 | 32.92 | 3.26 | 0.142 | 0.709491 | 0.000020 |
| BJ-Rain-15 | 8-13-2006 | 5.38 | 52 | 8.84 | 89.76 | 36.68 | 141.27 | 47.77 | 7.49 | 21.93 | 918.80 | 15.56 | 0.60 | 0.073 | 0.709678 | 0.000025 |
| BJ-Rain-16 | 8-26-2006 | 4.37 | 66 | 11.68 | 117.26 | 93.87 | 297.81 | 182.79 | 20.97 | 41.87 | 121.38 | 32.99 | 7.28 | 0.053 | 0.709791 | 0.000024 |

is an exceptant. We believe that there is a specific source of calcium such as calcite in the soil dust, causing high concentration of calcium in the high-deposition events. Arguments to support this hypothesis will be discussed in the following sections.

The volume-weighted mean (VWM) concentration was calculated for each ion, which is shown in Table 2. VWM was used to calculate the concentrations of ions in one-year period so it is able to account for the effect of precipitation amount on ion concentrations. It is shown in Table 2 that the concentrations of major ions are in the order of $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Cl}^- > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{F}^-$. Ca^{2+} is the most abundant ion among the cations, accounting for 69.3% of the total cations. NH_4^+ is the second abundant cation and contributes 21.2% of the cations measured. Among the anions, SO_4^{2-} , NO_3^- and Cl^- are the dominant ones. The VWM concentrations of SO_4^{2-} , NO_3^- and Cl^- are 315.79, 108.98, and 103.97 $\mu\text{eq l}^{-1}$, with maximum of 986.75, 381.52, and 216.36 $\mu\text{eq l}^{-1}$ in rainwater, respectively.

The pH values of rain samples range from 4.02 to 7.62, with the VWM value of 5.12, about 50% of the precipitations have pH values less than 5.0. According to previous studies, the naturally existing CO_2 , NO_x and SO_2 could be dissolved into the clouds and droplets, which would result in reducing pH values of rain in the clean atmosphere from 5.0 to 5.6 (Charlson and Rodhe, 1982; Galloway et al., 1993). Thus the rainwater samples with pH values less than 5.0 can be interpreted as the influence of anthropogenic derived pollutants while those with pH values more than 5.6 should indicate the presence of alkaline substances in the rainwater. The highest acidity was observed on 10th of July with a pH of 4.02, and the lowest one was recorded on 8th of August with a pH of 7.62. About one third of the rainwater samples had a pH less than 4.5 during the study period, which demonstrates unambiguous acid rain damage to the environment in Beijing.

4.2. Origins of major ions in the rainwaters

Atmosphere aerosols including sea salts, crustal dust, volcanic dust, biogenic material and anthropogenic emissions are the main sources of chemical compositions in rainwater, the chemical composition of rainfall is strongly affected by the chemical composition of the atmosphere (Roy and Negrel, 2001; Chetelat et al., 2005; Negrel et al., 2007). In order to find possible association between ions in precipitation, and consequently, the likely sources of pollutants, correlation coefficients (R^2) between ions in precipitation were calculated and presented in Table 3. Good correlation between SO_4^{2-}

and NO_3^- is expected because of the co-emission of their precursors SO_2 and NO_x , and the similarity of behavior in precipitation. There are good correlation between SO_4^{2-} and Ca^{2+} ($R^2 = 0.52$) and NH_4^+ ($R^2 = 0.91$), suggesting that Ca and NH_4^+ would play a major role in neutralizing acidic sulfur gas. NH_4^+ and SO_4^{2-} ($R^2 = 0.91$) are correlated more closely than that with NO_3^- ($R^2 = 0.53$). This indicates NH_3 will first react with H_2SO_4 and then the remaining NH_3 will be taken up by HNO_3 (Seinfeld, 1986). A careful check of Table 3 suggests that NaCl, NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, NH_4NO_3 , CaSO_4 are the predominant species combination. They may be formed in the atmospheric water droplets by aerosol scavenging and subsequent reaction of gaseous species.

To calculate the sea salt and terrestrial contributions for a given element, the main point to resolve is to select the reference species. Sodium has normally been used as a reference element for the sea-salt component. Magnesium is used mainly in coastal or marine rains (Berner and Berner, 1987). Chlorine has rarely been used. It could be used as a reference, however, if the Cl/Na ratios of rainwater do not differ from those of seawater (Negrel and Roy, 1998). The most useful or popular method of evaluating the contribution of sea-salt to ionic composition in precipitation is to compare the element-to- Na^+ ratios in rainwater to those in seawater (Negrel and Roy, 1998; Al-Khashman, 2005; Schmitt and Stille, 2005; Negrel et al., 2007). Fig. 2 provides element-to- Na^+ ratios (X/Na^+) of rainwaters from Beijing, and the dashed lines in the figure show X/Na^+ values in seawater. In Fig. 2a, only the ratio of one sample lies

Table 2
Mean concentration (in $\mu\text{eq l}^{-1}$) of major ionic composition and pH (in unit) along with statistical results in rainwaters.

| Component | VWM | Median | Mean | SD | Min | Max |
|---------------------------------|---------|--------|---------|--------|-------|---------|
| pH | 5.12 | 5.03 | 5.23 | 1.04 | 4.02 | 7.62 |
| EC | 76.88 | 78.00 | 84.63 | 54.55 | 13.00 | 254.00 |
| F ⁻ | 15.65 | 16.18 | 17.84 | 9.24 | 6.79 | 38.05 |
| Cl ⁻ | 103.97 | 108.17 | 117.42 | 30.46 | 84.99 | 216.36 |
| NO ₃ ⁻ | 108.98 | 114.37 | 142.37 | 102.32 | 30.31 | 381.52 |
| SO ₄ ²⁻ | 315.79 | 350.08 | 355.12 | 213.43 | 64.81 | 986.75 |
| NH ₄ ⁺ | 185.60 | 193.17 | 221.25 | 148.33 | 47.77 | 672.21 |
| K ⁺ | 17.65 | 17.76 | 21.74 | 12.98 | 3.83 | 49.61 |
| Na ⁺ | 24.96 | 25.39 | 36.66 | 40.67 | 3.78 | 179.93 |
| Ca ²⁺ | 607.19 | 255.16 | 478.83 | 487.46 | 14.49 | 1781.21 |
| Mg ²⁺ | 40.41 | 38.79 | 49.45 | 39.95 | 2.14 | 146.04 |
| (Σ^-) - (Σ^+) | -331.41 | 58.53 | -175.17 | | | |

VWM = volume-weighted mean; S.D. = standard deviation; Min = minimum; Max = maximum; (Σ^-) - (Σ^+) = sum of anions minus sum of cations.

Table 3

Matrix of correlation coefficients (R^2) of ionic concentrations (in $\mu\text{eq l}^{-1}$) in rainwater samples from Beijing.

| Ions | F ⁻ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | NH ₄ ⁺ | K ⁺ | Na ⁺ | Ca ²⁺ | Mg ²⁺ |
|-------------------------------|----------------|-----------------|------------------------------|-------------------------------|------------------------------|----------------|-----------------|------------------|------------------|
| F ⁻ | 1 | | | | | | | | |
| Cl ⁻ | 0.46 | 1 | | | | | | | |
| NO ₃ ⁻ | 0.82 | 0.71 | 1 | | | | | | |
| SO ₄ ²⁻ | 0.66 | 0.25 | 0.72 | 1 | | | | | |
| NH ₄ ⁺ | 0.55 | 0.11 | 0.53 | 0.91 | 1 | | | | |
| K ⁺ | 0.29 | 0.24 | 0.32 | 0.35 | 0.22 | 1 | | | |
| Na ⁺ | 0.24 | 0.91 | 0.54 | 0.14 | 0.03 | 0.15 | 1 | | |
| Ca ²⁺ | 0.37 | 0.08 | 0.37 | 0.52 | 0.42 | 0.03 | 0.08 | 1 | |
| Mg ²⁺ | 0.75 | 0.72 | 0.84 | 0.51 | 0.31 | 0.44 | 0.61 | 0.27 | 1 |

near the seawater line indicating that both Na and Cl in this sample came from sea salt. The facts that Cl/Na values of all the other rain samples are several times higher than that of seawater, indicating a significant anthropogenic Cl source. Chlorine cannot be used as a marine reference if anthropogenic sources exist. Fig. 2c illustrates the relationship between Na and Mg. All of ratios of rain samples studied lie well above the seawater line, reflecting the terrestrial influence on the Mg content reported by various authors (e.g., Berner and Berner, 1987; Negrel and Roy, 1998).

Sodium was used, therefore, as a marine tracer in rainwater. However, the selection of this element as a reference must be validated, particularly with regard to possible terrestrial influence. Since aluminum comes almost exclusively from terrestrial material,

the presence of terrestrial Na (Na_t) can be calculated according to the approach proposed by Negrel and Roy (1998):

$$\text{Na}_t = \text{Al}_{\text{rw}} \times (\text{Na}/\text{Al})_t \quad (1)$$

Hofmann et al. (1977) and Church et al. (1984) have shown that shales are more representative of average soils than rocks of the upper continental crust. Therefore, the correction of crustal Na with Al has been applied using shale as a terrestrial dust reference (Negrel and Roy, 1998). The Na/Al ratio of shale is 0.11. The correction of terrestrial Na with Al shows that less than 2% of Na is of terrestrial origin, except for No. 3 and 10 samples, in which terrestrial Na is close to 4%. This shows a minor contribution of the terrestrial component in Na content.

The proportions of sea salt and terrestrial end members were therefore calculated using Na as the marine reference species ($\text{Na}_{\text{ref}} = \text{Na}_{\text{rw}} - 0.11 \times \text{Al}_{\text{rw}}$). The contribution of terrestrial component for a given element X ($X = \text{Cl}^-, \text{SO}_4^{2-}, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$ and Sr^{2+}) is thus:

$$\text{X}_t = \text{X}_{\text{rw}} - \text{Na}_{\text{ref}} \times (\text{X}/\text{Na})_{\text{sw}} \quad (2)$$

The elemental ratios (X/Na) were determined according to the composition of seawater given by Berner and Berner (1987). The results, expressed in percentage, are given in Table 4. The proportions of Cl coming from non-sea-salt range from 4.8% to 94.9%. The non-marine input of Cl could come from various sources of pollution including automobile exhaust fumes, coal combustion and

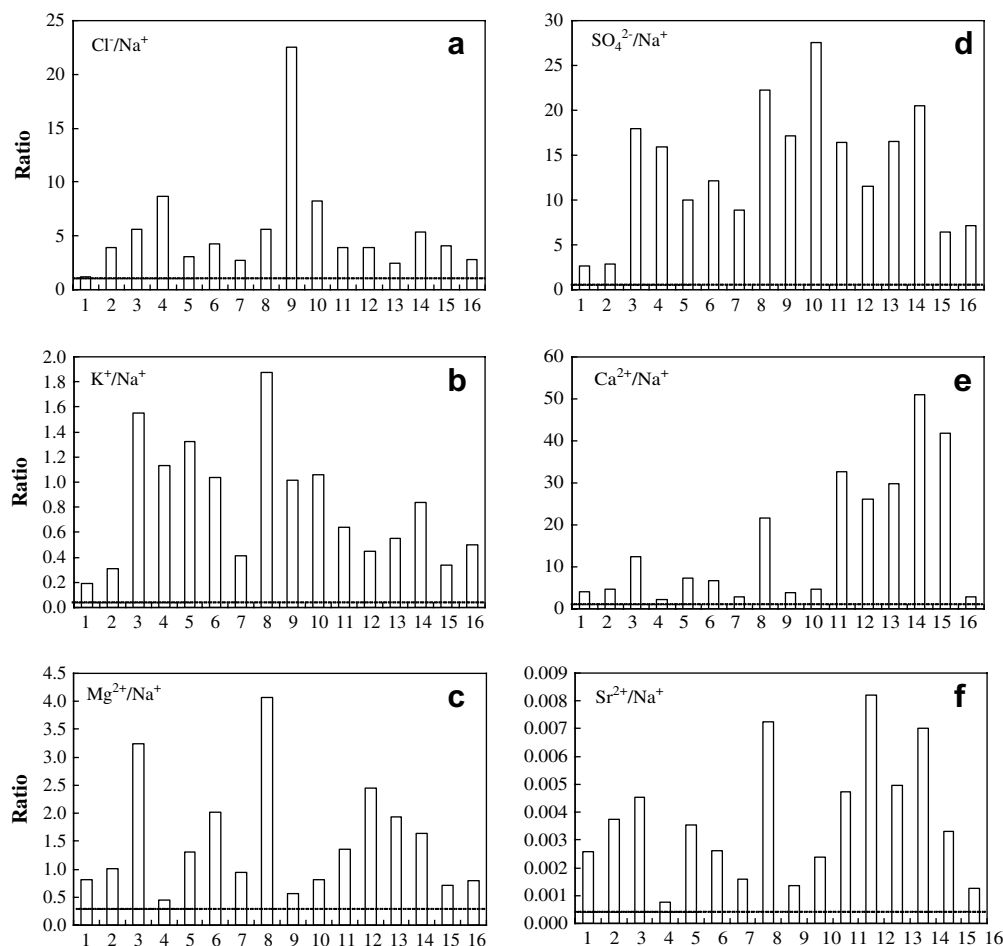


Fig. 2. Element-to- Na^+ ratios of rainwater composition (in $\mu\text{eq l}^{-1}$) from Beijing. The dashed lines in the figures (for Cl^- , SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} and Sr^{2+}) represent the value of X/Na in seawater (seawater data from Berner and Berner, 1987).

fertilizers. (Friedlander, 1973; Fuzzi et al., 1984; Negrel and Roy, 1998). SO_4^{2-} and NO_3^- are conventional acidic ions in precipitation. The non-marine input of SO_4^{2-} ranges from 95.7% to 99.6%. In China, coal accounts for about 70% of the commercial energy production, this leads to large emissions of SO_2 , which up to now has been the most important precursor of acid rain in China (Aas et al., 2007). NO_3^- in rainwater comes from both human activities (like fuel combustion) and chemical reactions in the atmosphere. The coal combustion will certainly produce a large emission of NO_x . A good correlation between SO_4^{2-} and NO_3^- ($R^2 = 0.72$) indicating their origin from similar sources, and reflects the input of pollutants from fossil fuel combustion.

Calcium is a dominant neutralizing cation and thus of importance to neutralizing acid rains (Nakano and Tanaka, 1997; Larssen and Carmichael, 2000). The Ca in rainwater from Beijing is mainly of terrestrial origin, marine Ca proportions are very low (<1.9%) for the whole data set (Table 4). In general, there are two major sources of terrestrial Ca in rainwater: (1) the local and remote transport of soil dust and/or carbonate weathering; (2) anthropogenic pollution (coal combustion, cement factories, etc). There are certain correlations among cations (K, Na, Ca, Mg, NH_4), which indicate that these elements have a common source (Table 3). These elements are common constituent of soil dust in Beijing area and in the arid and semi-arid regions in northern China (Feng et al., 2001; Yokoo et al., 2004). It is shown in Fig. 1 that Beijing city is surrounded by several desert and loess deposits, which cover very large areas. So we would suggest that the high content Ca in the rainwater is mainly due to the contribution of natural soil dust either from local or remote soil dust. Like Ca, Mg and K can also come from soil dust (Berner and Berner, 1987). Another source of these elements is probably anthropogenic pollution (industrial and agriculture activities) nearby the city. However, major element chemistry cannot precisely characterize the various end members. Therefore, Sr isotope compositions have been used to provide additional information of the different possible terrestrial sources in next section.

Atmospheric NH_3 also plays an important role in determining precipitation acidity. The presence of NH_3 is intimately related to the soil nature in the area of study. Volatilization of NH_3 increases as the soil pH value increases, and the pH values of soils in the Beijing region are around 7–8 (Zhao et al., 1988). The high level of NH_4^+ in rainwater coincides with the fact that the emission of ammonia to the atmosphere from agriculture activities is enormous in the Asian region, it is several times higher than that in North America and Europe (Galloway, 1995). So, it can be attributed the

presence of ammonium ions in the samples to a direct input of gaseous ammonia as well as to the input of absorbed ammonia from aerosols.

4.3. Strontium isotope constraints

Strontium isotope systematics can be used to investigate mixing of different sources of dissolved species in rain. Several researchers have reported concentrations and isotopic ratios of Sr and their results highlight the role of aerosol sources in the isotopic signature of rains (Herut et al., 1993; Nakano and Tanaka, 1997; Negrel and Roy, 1998; Schmitt and Stille, 2005; Chabaux et al., 2005; Negrel et al., 2007). The Sr concentrations of rainwater in Beijing show a range from 0.005 to $0.46 \mu\text{mol l}^{-1}$, whereas $^{87}\text{Sr}/^{86}\text{Sr}$ ratios span a range of 0.70912–0.71036. Fig. 3 shows the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios against element-to-Sr molar ratios (e.g. Ca/Sr, K/Sr) in rainwater. It is worth noting the lack of direct linear relationship among them, which could be argued for at least three sources of Sr in the rainwaters. Almost all of the samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than the seawater value (0.70917, Dia et al., 1992). This reflects a contribution from at least one more radiogenic Sr source. The most suitable candidate would be the Sr input of soil dust from local and distant continental bedrocks and soils, which are obviously more radiogenic. The isotopic compositions of Sr in dusts can be estimated by studying $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of river water and leaching experiments of soils with distilled water. Zhang et al. (1995) reported the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7111–0.7154 from rivers around the Taklimakan Desert in northwest China. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Huanghe river (Yellow River) also has the similar isotope ratio (0.7111; Palmer and Edmond, 1989). The leaching experiments on the loess and desert sands from the Central Loess Plateau in China show that water- and acetic acid-soluble minerals (mainly halite and calcite) have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7111 ± 0.0004 (Yokoo et al., 2004). It is noted that the rainwater samples with high Sr isotopic ratios (~ 0.710) were mainly collected during the months of May and June. That is a time of the windy and dusty seasons in Beijing area when the vegetations are much less developed. These sources can induce more radiogenic Sr, which would coincide with above interpretation. We adopt the Sr isotopic ratios (0.7111) as the natural soil dust end-member for the rainwater. The soil dust originates either from local or the desert and loess areas around Beijing and the transportation routes of soil dust have shown in Fig. 1.

Another non-sea-salt Sr source is probably made up of various anthropogenic inputs. Since the Sr isotope ratios of typical contaminant sources for the rainwaters collected in Beijing have not been characterized, the values from literatures can be used as the reference. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of fertilizer ranges from 0.7079 to 0.7087 (Negrel and Deschamps, 1996). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of automobile exhaust vary between 0.7077 and 0.7083, of urban heating between 0.7083 and 0.73335, of incinerators between 0.7097 and 0.7100 in the Paris atmosphere (Negrel et al., 2007). Although it is very difficult to identify the sources for Sr based on these data, it can be reasonably postulate that the anthropogenic end-member of big city (e.g. Beijing) are characterized by moderate $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and high K/Sr and Ca/Sr ratios (Fig. 3).

4.4. Acid neutralization and rain acidification

The observed concentrations of major ion and pH values in rainwater in Beijing have been compared with the available data from other urban areas in China and the world, which are presented in Table 5. Compared with those megacities in China, the data from Beijing show the highest ionic composition. The SO_4^{2-} of rainwater in Beijing is higher than those from most cities but lower than that of Chongqing and Chengdu, where both are located in the acid rain central zone in China. Compared with some sites in worldwide, the

Table 4
Proportions (in %) of the terrestrial contributions in the rainwater samples from Beijing city.

| Sample number | Cl^- (%) | SO_4^{2-} (%) | K^+ (%) | Na^+ (%) | Ca^{2+} (%) | Mg^{2+} (%) | Sr^{2+} (%) |
|---------------|-------------------|------------------------|------------------|-------------------|----------------------|----------------------|----------------------|
| BJ-Snow-1 | 4.8 | 95.7 | 88.7 | 1.8 | 98.9 | 72.6 | 92.6 |
| BJ-Snow-2 | 70.4 | 96.0 | 93.1 | 1.3 | 99.1 | 77.9 | 94.9 |
| BJ-Rain-3 | 79.9 | 99.4 | 98.7 | 4.2 | 99.7 | 93.3 | 95.9 |
| BJ-Rain-4 | 86.9 | 99.3 | 98.1 | 1.9 | 98.1 | 49.5 | 74.8 |
| BJ-Rain-5 | 62.8 | 98.8 | 98.4 | 1.9 | 99.4 | 83.0 | 94.6 |
| BJ-Rain-6 | 72.8 | 99.0 | 97.9 | 0.2 | 99.4 | 88.8 | 92.6 |
| BJ-Rain-7 | 57.2 | 98.7 | 94.7 | 0.4 | 98.5 | 76.2 | 87.8 |
| BJ-Rain-8 | 79.2 | 99.5 | 98.8 | 0.3 | 99.8 | 94.4 | 97.3 |
| BJ-Rain-9 | 94.9 | 99.3 | 97.9 | 1.0 | 98.9 | 60.5 | 86.0 |
| BJ-Rain-10 | 86.4 | 99.6 | 98.0 | 3.9 | 99.1 | 72.9 | 92.3 |
| BJ-Rain-11 | 70.1 | 99.3 | 96.6 | 0.1 | 99.9 | 83.4 | 95.9 |
| BJ-Rain-12 | 70.6 | 99.0 | 95.2 | 1.2 | 99.8 | 90.8 | 97.7 |
| BJ-Rain-13 | 52.6 | 99.3 | 96.0 | 0.2 | 99.9 | 88.3 | 96.1 |
| BJ-Rain-14 | 78.6 | 99.4 | 97.4 | 1.8 | 99.9 | 86.4 | 97.3 |
| BJ-Rain-15 | 71.6 | 98.2 | 93.6 | 0.3 | 99.9 | 68.2 | 94.2 |
| BJ-Rain-16 | 59.2 | 98.4 | 95.7 | 1.9 | 98.5 | 71.8 | 85.1 |

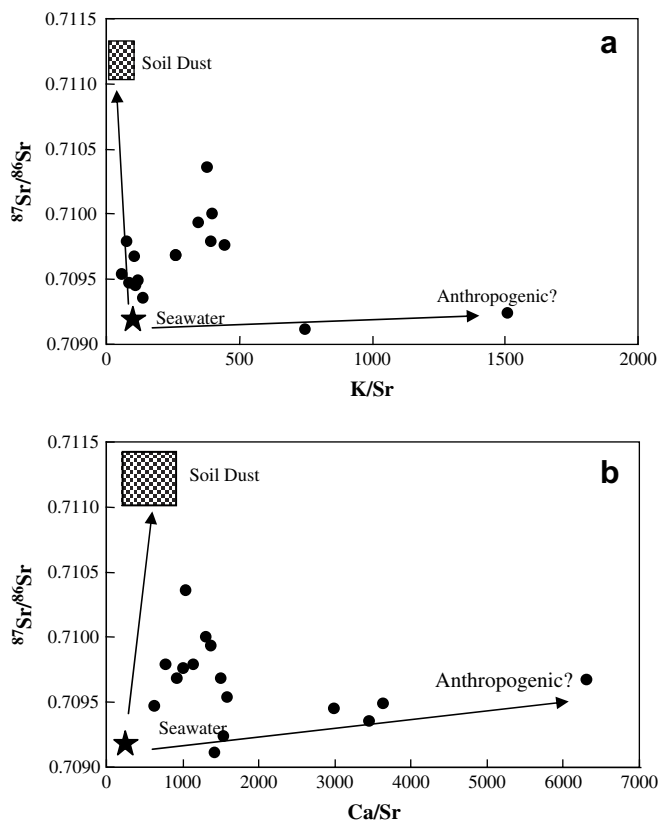


Fig. 3. Variation of Sr isotope ratios against K/Sr (a) and against Ca/Sr (b) molar ratios in the rainwater samples. The characteristic values of soil dust and anthropogenic inputs are discussed in the text for detail.

ion concentrations of Beijing rainwater, especially SO_4^{2-} , NO_3^- , Ca^{2+} and NH_4^+ , consumedly exceed than those of reference cities in Europe, American and East Asia. All these results indicate Beijing has been a severe polluted city over the world. In generally,

precipitation acidity is heavily governed by the relative contribution of Ca^{2+} , NH_4^+ , SO_4^{2-} and NO_3^- . As mentioned above, Beijing's rainwater has a high SO_4^{2-} concentration, and the NO_3^- concentration is also found to be the highest one over the world cities (Table 5). However, compared with these acid rain areas in the world, the problem of acid rain is not serious in Beijing. This is consistent with the fact that Beijing city is surrounded by some desert and loess areas. The soil dust from these areas can contribute a large amount of alkaline material to precipitation and to neutralize the acidic ions. From Table 5, it can be observed that the concentrations of alkaline ions (Ca^{2+} , Mg^{2+} , NH_4^+ , etc.) of rainwater in Beijing are higher than those reported for other sites. Therefore it is clear that the existence of acid rain depends not only on the presence of acidic ions in the precipitation, but also upon other factors such as the amount of alkaline material available as a neutralizing agent.

In comparison the data of this present work with those suggested by Zhao et al. (1988) in Table 5, it is noteworthy that the tendency of rain acidification in precipitation in Beijing is obvious, and the pH value has been reduced by 1.5 units since 1980s. It is also observed that the concentrations of SO_4^{2-} and NH_4^+ have varied within a very limited range, whereas NO_3^- has increased greatly from 81 to 142 $\mu\text{eq l}^{-1}$, and Ca^{2+} has decreased greatly from 760 to 479 $\mu\text{eq l}^{-1}$ during the same period. As previous discussion, Ca^{2+} is mainly attributed to the dissolution of calcite in natural soil dust from arid and semi-arid areas in northern China. In order to improve air quality in Beijing, the Chinese government has taken some powerful measures (e.g. natural forest protection project, converting cropland for forest and grassland, and restriction of uncontrolled grazing) to control sand-dust storm in northwest China since 1990s. These environmental protection and control measures have reduced greatly the frequency and intensity of sand-dust storms. At the same time the concentrations of alkaline ions (especially Ca^{2+}) have also been reduced in the atmosphere. Meanwhile, the amount of private car now has exceeded 3.2 million and increased quickly during the last decade in Beijing. The rapid increasing of vehicles from motorization has resulted in high emission of SO_x and NO_x and formed the high content of acidic ions. It can be concluded that both increase of the acidic ions

Table 5

Comparison of the major ions concentration (in $\mu\text{eq l}^{-1}$) in Beijing with other sites in China and worldwide.

| Region | pH | Cl^- | NO_3^- | SO_4^{2-} | NH_4^+ | K^+ | Na^+ | Ca^{2+} | Mg^{2+} |
|----------------------------------|------|---------------|-----------------|--------------------|-----------------|--------------|---------------|------------------|------------------|
| Beijing ^a | 5.23 | 117.4 | 142.4 | 355.1 | 221.2 | 21.7 | 36.7 | 478.8 | 49.5 |
| Beijing ^b | 5.12 | 104 | 109 | 315.8 | 185.6 | 17.6 | 25 | 607.2 | 40.4 |
| Beijing ^{c,a} | 6.74 | 59.1 | 81 | 337.5 | 224.4 | 38.2 | 77.4 | 760 | |
| Chengdu ^{d,b} | 4.4 | 42.3 | 30.4 | 431.5 | 250.7 | 20.8 | 22.6 | 192 | 33.2 |
| Chongqing ^{d,b} | 4.6 | 40.3 | 43.2 | 421.8 | 386.6 | 15.2 | 39.8 | 207.2 | 13.2 |
| Guiyang ^{e,a} | 4.53 | 21.2 | 48.2 | 188 | | 11 | 4 | 113.2 | 25.5 |
| Changsha ^{f,a} | 4.32 | 9.6 | 21.8 | 143 | 70.4 | 3.8 | 3.9 | 62 | 5.6 |
| Nanjing ^{f,a} | 5.09 | 154 | 34.5 | 212 | 289 | 10.5 | 13 | 287 | 30 |
| Shanghai ^{g,b} | 4.49 | 58.3 | 49.8 | 199.6 | 80.9 | 14.9 | 50.1 | 204 | 29.6 |
| Tokyo (Japan) ^{h,b} | 4.52 | 55.2 | 30.5 | 50.2 | 40.4 | 2.9 | 37 | 24.9 | 11.5 |
| Massif (France) ^{i,a} | 5.22 | 19.6 | 36.2 | 22.3 | | 5.7 | 14.4 | 14.6 | 3.4 |
| Istanbul (Turkey) ^{j,b} | 4.81 | 124.8 | 33.4 | 115.2 | 12.8 | 57.4 | 75.2 | 285 | 99.6 |
| Itatiaia (Brazil) ^{k,b} | 4.94 | 5.2 | 11.8 | 15.5 | 13.5 | 1.3 | 3.9 | 4.3 | 2.2 |
| Mexico (Mexico) ^{l,b} | 5.08 | 9.6 | 42.6 | 61.9 | 92.4 | 2.2 | 7 | 26.4 | 2.5 |

^a Arithmetic means.

^b volume-weighted means.

^c Zhao et al. (1988).

^d Lei et al. (1997).

^e Han and Liu (2006).

^f Zhang et al. (2007).

^g Huang et al. (2008).

^h Okuda et al. (2005).

ⁱ Negrel and Roy (1998).

^j Basak and Alagha (2004).

^k Mello and Almeida (2004).

^l Baez et al. (2007).

concentrations and decrease of the alkaline ions (mainly Ca^{2+}) concentration have resulted in the rain acidification tendency of rainwater in Beijing.

5. Conclusion

The chemical and Sr isotope compositions of rainwaters in Beijing, the most important city in China, were analyzed on the basis of monitoring an urban site over a period of one year. We attempt to identify the origins of major ions by using the combination of statistic analyses methods and strontium isotope systematics. It is suggested that SO_4^{2-} , NO_3^- and Cl^- mainly come from anthropogenic activities (fossil fuel combustion, automobile exhaust and fertilizers). Ca^{2+} is mainly due to the contribution of calcite in natural soil dust transported either from local or from desert and loess areas in northern China.

The Sr concentrations vary from 0.005 to 0.46 $\mu\text{mol l}^{-1}$, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios varied during a small range (0.70912–0.71036) in the rainwater samples. Almost all of the samples have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than that of seawater. Covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with the related element ratios in the rainwater would suggest presence of at least three sources of Sr in the rainwaters. Such sources include sea salts ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.90917$), soluble soil dust minerals originating either local or the desert and loess areas (~ 0.7111), and anthropogenic sources (coal combustion, automobile exhausts and fertilizers).

Beijing rainwaters show very high concentrations of acidic ions (SO_4^{2-} and NO_3^-). However, compared with these acid rain areas in the world, the problem of acid rain is not very serious in Beijing. It is suggested that the higher concentrations of alkaline ions (mainly Ca^{2+}) in the atmosphere neutralize the acidity of acid rain caused by sulfuric acid and nitric acid from fossil fuel combustion and automobile exhaust. It is noteworthy that the acidification trend of rainwater in Beijing is obvious, and the pH value has reduced by 1.5 units since 1980s. The large emission of SO_2 from coal combustion still is the most important precursor of acid rain up to now in China. However, according to this study, the increase of NO_x emission from the automobile exhaust is becoming another important cause of the acid rain, especially in some megacities. It should be kept in mind that the contribution of nitrate to acid deposition will be more significant. Thus, the attention should be more focused on nitrogen species, and a further integrated approach is required to address the acid precipitation problem in China.

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