



Rare earth elements concentrations and speciation in rainwater from Guiyang, an acid rain impacted zone of Southwest China



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ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form 29 August 2016

Accepted 31 August 2016

Available online 1 September 2016

Keywords:

Rare earth elements

Concentration

Speciation

La anomaly

Acid rain

ABSTRACT

Rare earth elements (REEs) and major ions were determined in rainwater samples collected from Guiyang in the acid rain impacted zone of Southwest China. The concentrations of total dissolved and acid-soluble REEs in rainwater are higher than those of most of the world's cities as well as the local surface water. The dissolved REE concentrations are negatively correlated to pH in rainwater. This is consistent with acidification of rainwater resulting in increasing REE concentrations. Speciation calculations using the PHREEQC-Model predict that the free REE metal ion (i.e., Ln^{3+}), sulfate (LnSO_4^+), oxalate (LnOx^+ and LnOx_2^-) and fluoride (LnF^{2+}) complexes were relatively important forms of dissolved REE. Although the contribution to rainwater acidity of oxalic acid is much lower than that of sulfuric acid, the proportion of REE-oxalate complexes is not lower than that of REE-sulfate complexes in rain waters. The rainwater is enriched in the middle REEs (MREE) compared to both the light REEs (LREE) and heavy REEs (HREE). REE-phosphate complexes, phosphatic minerals and a Fe-Mn-oxyhydroxide coating are more likely controls on the development of MREE enrichment in the rainwater. Complexation of sulfate and REE played little role in the development of MREE enrichment, even though sulfate is the most important anion in acidic rainwater. In the shale-normalized REE pattern plot, La showed a clear positive anomaly. La might have two main anthropogenic sources in rainwater. One of the important sources could be automobile emission; another main source of excess La in rainwater could be the REE fertilizer that has been widely used in the agriculture of China for approximately 30 years.

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1. Introduction

Due to their unique chemical and physical properties, REEs have been extensively used as powerful tracers of material sources and geochemical processes in oceans, rivers, estuaries, lakes and groundwater (Elderfield et al., 1990; Sholkovitz, 1995; Gabrielli et al., 2009; Johannesson et al., 2011; Pearce et al., 2013). It has recently been recognized that REEs in atmospheric particles and rainwater have a significant impact on the geochemical cycle of REEs in the hydrosphere (Greaves et al., 1994, 1999; Wilkinson et al., 1997; Wang et al., 2000; Yang et al., 2007; Schacht et al., 2010; Suzuki et al., 2011; Klaver et al., 2014; Inguaggiato et al., 2016).

The REEs are commonly divided into three groups: light rare earth elements (LREE) from La to Nd, middle rare earth elements (MREE) from Sm to Dy, and heavy rare earth elements (HREE) from Ho to Lu (Inguaggiato et al., 2016). Shale-normalized REE patterns are often used to determine the source of REEs in rainwater and the behavior of REEs in aerosol/precipitation systems. Broadly, four main types of shale-normalized patterns are identified from the data obtained for

the dissolved REEs in rainwater. The first type is enriched in MREE as shown, for example, by REE pattern of rainwater from the Bermuda, Lewes (Delaware), and Woods Hole (Massachusetts). Rainwater from Sagami-hara (Japan) was also enriched in some acid-soluble MREE (Sholkovitz et al., 1993; Shimamura et al., 2007). The second type is characterized by flat REE patterns such as in rainwater of suburban Tokyo, Anmyeon Island (Yellow sea) and Seoul (Ryu et al., 2007; Iwashita et al., 2011; Soyol-Erdene et al., 2011). This type also includes patterns slightly enhanced in either LREE or HREE. The shale-normalized ratios between the REEs in this flat type pattern are not absolutely equal. For example, the rainwater at Anmyeon Island was slightly enriched in LREE, while rainwater in Seoul exhibited a slightly HREE-enriched shale-normalized pattern. As a result, the LREE were preferentially adsorbed/desorbed from atmospheric particles. The third type is the HREE-enrichment pattern. Aubert et al. (2002) found that rainwater and snow from east France showed HREE enrichment similar to seawater. This shale-normalized pattern was commonly detected in natural waters with high carbonate or CO_2 concentration (Johannesson and Lyons, 1994; Choi et al., 2009; Inguaggiato et al., 2016). The enrichment in HREE is the result of the formation of stable carbonate complexes in water where HREE preferentially form stronger carbonate complexes than MREE and LREE (Elderfield, 1988; Goldstein and Jacobsen, 1988a

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and 1988b). The last type is the LREE enrichment pattern; this shale-normalized pattern is rare in natural waters. The two smaller rivers from the Archean terrains, the Great Whale River and Lake Isua were strongly enriched in LREE (Goldstein and Jacobsen, 1988a, 1988b). Rainwater from the East China Sea, Nakaminato (Japan) and Chofu (Japan) also showed enrichment in LREE compared to HREE. This may have occurred because LREE are more soluble than HREE in airborne particles or more LREE relative to HREE may exist in the exchangeable phase of airborne particles (Zhang and Liu, 2004). In addition, large La, Eu, and Gd anomalies were also noted in rainwater. Sholkovitz et al. (1993) first reported large negative Eu anomalies in rainwater from the American east coast. Rainwater from Tokyo and Seoul exhibited small positive Eu anomalies (Shimamura et al., 2007; Soyol-Erdene et al., 2011). The common valence of Eu is the trivalent oxidation state. Under high temperature and pressure conditions, Eu can be reduced from Eu(III) to the Eu(II). Variation of Eu has frequently been observed in hydrothermal waters and mantle-derived magmatic rocks (Elderfield, 1988; Klinkhammer et al., 1994; Douville et al., 1999; Schmidt et al., 2007; Hongo et al., 2007; Bau et al., 2010; Craddock et al., 2010). To date, the reduction of Eu(III) to Eu(II) has not been reported in low temperature surface waters. The Eu anomalies in rainwater are geologically inherited through chemical weathering of rocks and minerals. In the crustal-normalized REE pattern plot, La and Gd in rainwater from Tokyo showed clear positive anomalies (Shimamura et al., 2007). The cracking catalyst for petrol refining and Gd-DTPA (Gadolinium diethyltriaminepentaacetic acid) used for Magnetic Resonance Imaging (MRI) contrast agents may

be the main anthropogenic source for rainwater (Kitto et al., 1992; Nozaki et al., 2000; Kulkarni et al., 2007; Kulaksız and Bau, 2013). Although studies have investigated REEs in dry or wet deposition, their results are not sufficient to understand REE behavior in rainwater. In this paper, we report the REE concentrations in rainwater from Guiyang to achieve a better understanding of the distribution and speciation of REEs in rainwater and sources of anthropogenic La.

2. Brief description of study area

Guizhou province is situated along the eastern slopes of the Yunnan-Guizhou Plateau, which is the transition zone between the eastern plains and western plateaus. It has a mountainous topography and cities there are often located in basins surrounded by high mountains. Guiyang city (26°11'–27°22'N, 106°07'–107°17') is located in central Guizhou province (Fig. 1). The annual average precipitation in Guiyang city is 1111.7 mm, 75% of which occurs in summer. The number of rainy days per year can be as high as 174.1 with >10 rainfall days per month. However, rainfall is very low on most rainy days. Guiyang is an industrial and economic center of Guizhou province, with a land area of 8034 km² and a population of >3.37 million people. Twenty percent of the aluminum in China is processed in Guiyang, and one of the three largest phosphate mines in China is located in the city (Xiao and Liu, 2004). Due to the climate and topography, the atmosphere circulation of Guiyang is relatively closed, making the air pollution difficult to dilute. Guiyang is a typical acid rain impacted zone in China (Zhao et al.,

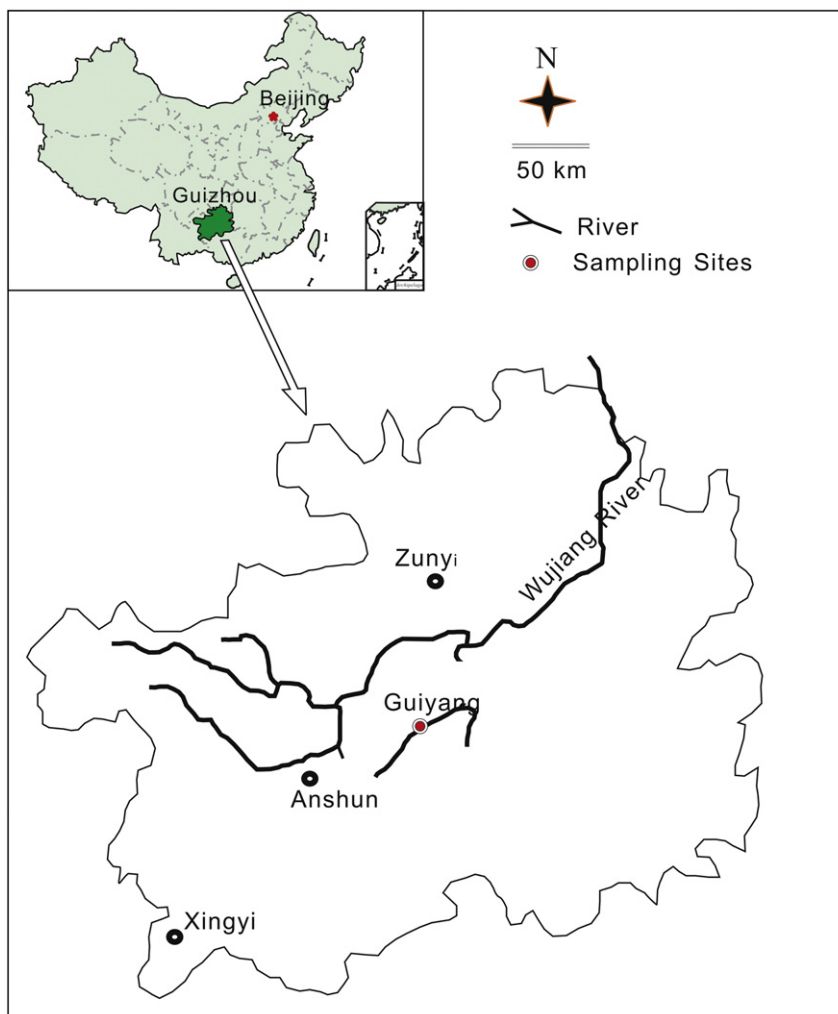


Fig. 1. Simplified map of sampling location.

1988; Tang et al., 1995; Han and Liu, 2006; Han et al., 2011). The weighted average pH of the precipitation was 4.43 from 2005 to 2010, which is less than the acid rain threshold of 5.60 (Luo et al., 2013).

3. Materials and methods

3.1. Sampling and analytics

The sampling site is located at an elevation of 1071 m, with no nearby pollution source or adjacent obstructions. The samplers are 5-L high-density polyethylene jars that were located 1 m above the roof. To prevent contamination from the samplers, they were cleaned with 5–7 N HNO₃, rinsed with Milli-Q water and dried. To avoid the influence of dry precipitation, we collected bulk rainwater samples half an hour after the start of each rain event. Because measuring the REE concentrations in rainwater requires approximately two liter samples, only rainfall from events of >5 mm were collected. A total of 20 samples were collected during the period from April to December 2006. For the determination of REEs in rainwater in December, the rainwater samples were collected from the total precipitation of three days from 28 to 30 December because the rainfall events were too small during that month. The pH values of rainwater were measured in situ with a portable pH meter (Sens Ion⁺, Hach). The samples were filtered through 0.22- μ m membrane filters immediately after collection. An aliquot of 10 mL was used to measure the major anions using an ion chromatograph (ICS-2000, Dionex). An aliquot of 10 mL was acidified to pH \leq 2, which was used to measure the major cations with an Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES, Vista MPX, Varian). The remainder of the filtered sample was acidified to a pH of 1.5 for the determination of the dissolved REE. Simultaneously, a 1-L unfiltered water sample was acidified to a pH of 1.5 using ultrapure HCl immediately after collection and filtered through 0.22- μ m filters after 2 weeks for the acid-soluble REE determination. The method for determining REEs is similar to that described by Shabani et al. (1990) using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Elan 9000, Perkin Elmer). All samples were pre-concentrated in a class 1000 clean room of the State Key Laboratory of Environmental Geochemistry (Guiyang, China) before measurement. The pre-concentrated procedure was performed as follows (Shabani et al., 1990; Wang et al., 2013): REEs were extracted from 1 L of rainwater with a mixture of 65% HDEHP (2-

ethylhexyl hydrogen phosphate) and 35% H₂MEHP (2-ethylhexyl dihydrogen phosphate) in heptanes, then back-extracted with octyl alcohol and ultrapure HCl and evaporated to dryness, and finally transformed into a 3% ultrapure HNO₃ solution for ICP-MS analysis. By using this method, the REE concentrations in solution were approximately 200 times higher than those in rainwater. Indium was added to all samples as an internal standard to control the recovery rate of REEs during the pre-concentrated procedure. Rhodium was also added to monitor the stability of the ICP-MS.

The recovery values of the purification and concentration procedure for REEs and the internal standard are >98%. The multi-element standard solutions for ICP-MS were purchased from SPEX Industries, Inc., and are accurate to \pm 0.5% for each REE. Replicate analyses (five times) of the surface water from Lake Aha (local surface water) give relative standard deviations of approximately 10% for Ce, 5% for LREE, and <3% for HREE.

3.2. Speciation modeling

The free ion species (Ln³⁺, where Ln stands for the entire lanthanide series elements) is not the only species of REEs in water, as many other REE complexes also exist in solution (Lee and Byrne, 1992; Johannesson and Lyons, 1995; Johannesson et al., 1996, 2004, 2011; Schijf and Byrne, 2001; Marsac et al., 2011). The kind and concentrations of REE vary in different types of water. Until now, the speciation of REE in rainwater has not been reported. Here, the REE speciation of rainwater calculations were performed using PHREEQC (version 2.18.00), developed by Parkhurst and Appelo (1999). PHREEQC is based on an ion-association aqueous model and is designed to perform speciation and saturation-index calculations. In addition, we updated PHREEQC “minteq.v4” database by incorporating new stability constants for Ln(SO₄)⁺, Ln-Oxalate⁺ (LnOx⁺), Ln(Oxalate)₂⁻ (LnOx₂⁻), LnF²⁺, Ln-Acetate²⁺ (LnAC²⁺), LnCl²⁺, Ln-Formate²⁺, LnNO₃⁺, LnOH²⁺, LnHPO₄⁺, LnH₂PO₄⁺, and LnPO₄. The stability constants for REE-ligand used in this work are obtained from Lee and Byrne (1992), Millero (1992), Schijf and Byrne (2001) and Martell et al. (2004).

The rainwater temperature could not be accurately measured because it varied from high altitude to the ground and from day to night. Fortunately, the solution temperature plays a minor role in determining the speciation of the REEs (Johannesson et al., 1996). Thus, the average

Table 1
Dissolved concentration (in pmol/kg) of rare earth elements in rain waters.

	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Gd/Nd) _{SN}	(Gd/Yb) _{SN}	La/La*	Σ REE
20060410	3.38	779.7	1515	200.5	842.5	162.6	34.94	167.1	23.41	141.5	22.18	69.50	9.26	60.13	8.32	1.36	1.50	1.02	4037
20060424	3.97	442.5	752.0	97.26	373.4	67.24	14.44	70.92	9.70	58.14	8.91	27.18	3.37	19.48	2.72	1.30	1.97	1.00	1947
20060425	3.95	607.8	1158	165.6	647.3	137.6	30.34	148.4	20.36	118.3	18.53	56.23	7.13	44.03	6.35	1.58	1.82	0.83	3166
20060509	5.86	100.5	145.7	19.03	78.73	13.44	3.08	15.36	2.02	12.41	2.10	6.82	0.85	5.62	0.88	1.34	1.48	1.34	406.5
20060513	5.48	670.0	735.1	88.08	327.5	40.98	8.31	49.74	5.75	32.13	5.62	17.66	2.10	12.18	1.72	1.04	2.21	1.58	1997
20060526	5.66	218.5	506.6	77.78	341.2	73.40	16.78	76.67	10.19	62.32	10.49	33.48	4.40	29.33	3.99	1.54	1.41	0.81	1465
20060622	4.36	1188	1900	254.4	991.9	179.0	40.15	194.1	25.36	153.5	24.04	74.35	9.59	65.35	8.42	1.34	1.61	1.05	5108
20060707	5.46	281.1	242.6	35.53	145.9	23.09	4.92	24.48	3.14	19.11	3.13	11.06	1.50	9.74	1.48	1.15	1.36	1.97	806.8
20060714	4.24	539.3	738.5	99.23	385.7	68.40	15.26	72.21	9.67	57.00	8.82	26.40	3.33	20.59	2.81	1.29	1.90	1.22	2047
20060716	5.95	363.1	479.5	59.87	226.1	40.20	8.57	45.46	6.13	37.43	6.16	18.83	2.39	15.60	2.06	1.38	1.58	1.29	1311
20060718	5.91	308.0	501.2	68.35	269.3	52.20	11.95	55.59	7.60	46.21	7.41	23.01	2.87	17.30	2.42	1.42	1.74	1.03	1373
20060730	4.36	496.0	747.9	92.30	348.0	60.60	13.11	71.56	9.74	59.38	9.90	31.00	4.07	26.02	3.53	1.41	1.49	1.14	1973
20060801	5.70	441.4	456.4	60.18	236.5	43.92	9.24	46.56	6.10	38.93	6.37	20.14	2.72	18.23	2.54	1.35	1.38	1.68	1389
20060806	5.67	172.0	356.6	47.02	232.5	49.72	11.87	53.32	7.05	45.11	8.27	27.63	4.03	27.09	4.27	1.58	1.06	1.58	1046
20060807	5.82	264.6	455.6	62.57	264.0	52.26	12.45	61.25	8.74	54.50	9.06	27.86	3.72	23.49	3.42	1.59	1.41	1.12	1303
20060822	5.98	383.4	563.0	84.28	254.0	48.75	10.39	51.11	7.18	44.87	7.24	23.80	3.41	22.31	3.21	1.38	1.24	0.73	1507
20060908	5.34	250.5	510.0	64.37	210.7	41.60	8.75	41.92	5.59	32.62	5.00	15.88	2.04	12.52	1.78	1.37	1.81	0.68	1203
20061008	4.40	1059	1426	192.3	747.9	140.3	30.19	147.3	19.75	121.3	19.18	59.24	7.74	49.80	7.09	1.35	1.60	1.23	4028
20061018	4.07	1212	1309	177.6	655.6	132.3	30.92	147.1	19.85	122.0	20.03	61.99	8.00	50.48	7.00	1.54	1.58	1.41	3954
20061114	4.01	908.3	1733	246.3	991.2	218.0	50.17	236.0	33.07	205.6	32.81	101.0	13.40	84.91	12.14	1.64	1.50	0.88	4866
20061230	3.92	860.5	601.0	72.90	261.2	41.86	8.60	46.54	6.41	40.66	6.57	21.28	2.77	17.50	2.54	1.22	1.44	2.32	1990

Samples are identified by the sampling date that expressed as year, followed by month and day. La/La* = La_{SN}/(3Pr_{SN} - 2Nd_{SN}). See text for discussion.

temperature of the day when the rainwater sample was collected was used in the speciation calculations.

4. Results and discussion

4.1. pH and major ion concentration variations

The pH ranges from 3.38 to 5.98 in rainwater collected from Guiyang (Table 1). The pH of 62% of samples is lower than 5.6 and that of other samples ranges between 5.60 and 5.98 in Guiyang in 2006. The frequency and intensity of acid rain are relatively lower than in the 1980s and 1990s (Zhao et al., 1988; Han and Liu, 2006). The pH values of most rainwater in Guiyang are significantly <5.6 from September to April of the next year (autumn, winter and early spring). The pH values from May to August (later spring and summer) are relatively high, and more than half of the rainfall events have pH values > 5.6.

Seven major ions in the samples from August to December were measured (Table 2 and Fig. 2). Ca^{2+} is the dominant cation in rainwater. Its concentration ranges from 86.4 to 174 $\mu\text{mol/kg}$, with a mean concentration of 126 $\mu\text{mol/kg}$. Although, NH_4^+ was not measured, the NH_4^+ content was higher than that of the other cations, except for Ca^{2+} (Xiao et al., 2010; Han et al., 2011). It accounted for approximately 29% of the total mass of cations (Xiao et al., 2010). The mean concentrations of Mg^{2+} , K^+ and Na^+ are low, 18.2, 8.28 and 8.89 $\mu\text{mol/kg}$, respectively. SO_4^{2-} is the most abundant anion. Its concentration ranges from 98.0 to 244 $\mu\text{mol/kg}$, with a mean concentration of 115 $\mu\text{mol/kg}$. The calculated percentage of seawater salinity for these rainwater samples shows that the source of SO_4^{2-} is mostly non-marine. This result is consistent with that of earlier studies (Xiao and Liu, 2004; Han and Liu, 2006). These studies considered that the SO_2 released from coal-fueled industries was the key source of SO_4^{2-} , and it was also the main cause of acid rain (Xiao and Liu, 2004). The NO_3^- and Cl^- concentrations are lower than that of SO_4^{2-} , 71.2 and 46.2 $\mu\text{mol/L}$, respectively. It should be noted that carboxylic acids in the rainwater from Guiyang were important, accounting for approximately 18.7% of the free acidity and oxalic, acetic and formic acids accounted for 6.1% (0%–89.4%), 4.7% (0%–98.4%), 7.9% (0%–97.2%), respectively (Xu et al., 2010). The direct emission from vehicles, biomass burning, soils and the photochemical reaction of unsaturated hydrocarbons in the atmosphere were considered as major sources of carboxylic acids (Xu et al., 2010). HCO_3^- is important in most natural water; however, it can be neglected in Guiyang because the rainwater is weakly acidic.

4.2. REE concentrations in rainwater

The REE concentrations are significantly variable in the rainwater collected from different rainfall events (Fig. 3 and Tables 1, 3). The total dissolved REE (ΣREE) concentrations range from 402 to 5052 pmol/kg , with a mean concentration of 2208 pmol/kg . The total dissolved REE concentrations in rainwater are relatively low during the period from May to September, that is, between 400 and 2100 pmol/kg , except for the sample collected on June 22. The total

dissolved REE concentrations are high during the period from October to April, that is, between 1900 and 5100 pmol/L . The total acid-soluble REE (ΣREE) concentrations range from 1073 to 5743 pmol/kg , with a mean concentration of 2615 pmol/kg . The total acid-soluble REE concentrations in rainwater are relatively low during the period from July to September, that is, between 1000 and 2300 pmol/kg . The total acid-soluble REEs are high during the period from October to December and from April to June, that is, between 2100 and 5700 pmol/kg , except for the sample collected on May 9. The concentrations of total dissolved REE are significantly lower than those of acid-soluble REE, accounting for 26.0%–98.8% (Table 3).

The concentrations of dissolved and acid-soluble REEs in rainwater from other cities in the world are presented as shale-normalized plots in Fig. 4. The lowest total REE concentrations (39.93 and 63.86 pmol/kg , respectively) were found in the rainwater samples from Woods Hole and Vosges Mountains (Sholkovitz et al., 1993; Aubert et al., 2002). The concentrations of total dissolved REEs in rainwater from Anmyeon Island, Seoul, East China Sea, Nakaminato, Tokyo, and the Alps and total acid-soluble REEs in rainwater from Sagami-hara, Bermuda, and Lewes were between 100 and 1000 pmol/kg (Sholkovitz et al., 1993; Aubert et al., 2002; Zhang and Liu, 2004; Ryu et al., 2007; Shimamura et al., 2007; Soyol-Erdene et al., 2011). The concentrations of total dissolved REEs in rainwater from Strasbourg, Chofu, and Sagami-hara ranged from 1000 to 2000 pmol/kg (Aubert et al., 2002; Zhang and Liu, 2004; Iwashita et al., 2011). The total dissolved and acid-soluble REE concentrations in rainwater from Guiyang are detected at the highest level, with mean concentrations of >2000 pmol/kg . Although the concentrations of the total REEs in rainwater from Guiyang are higher than in any other city, the HREE abundance does not reach that of HREE in rain water from Strasbourg. The concentrations of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu in rainwater collected in Strasbourg were all higher than in rainwater collected in Guiyang on June 22, that is, when the highest REEs concentration is detected in all samples in Guiyang. It should be noted that the patterns of REEs between Guiyang and Strasbourg are different. The rainwater from Guiyang is enriched in MREE, whereas that from Strasbourg was enriched in HREE. The main sources of dissolved solids in rainwater are atmospheric particles, including marine, anthropogenic, and terrigenous particles (Galloway et al., 1982; Chester et al., 1994; Lim and Jickells, 1994; Halstead et al., 2000; Roy and Negrel, 2001; Negrel et al., 2007). Terrestrial sources include crustal dust, volcanic dust and biogenic material. Anthropogenic sources include coal dust and other fine particles that are generated by fossil fuel consumption. The chemical compositions of airborne particles from different sources are clearly different. Therefore, the species and amounts of airborne particles could be the primary factor in controlling the REE concentration in rainwater. The total dissolved REE concentrations increased with decreasing pH were observed in the world's major rivers and hydrothermal system (Colombia) (Fig. 3). This demonstrates that decreasing pH can lead to increasing dissolved REE concentrations in solutions (Goldstein and Jacobsen, 1988a, 1988b; Inguaggiato et al., 2015). A similar phenomenon is also found in rainwater from Guiyang. Therefore, another important factor affecting the REE

Table 2
The chemical compositions of major species in rainwaters from Guiyang ($\mu\text{mol/kg}$).

	T(°C)	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	PNSS% ^a	F^-	HCOOH^b	CH_3COOH^b	$\text{H}_2\text{C}_2\text{O}_4^b$
2006.8.22	20	10.2	15.0	136	27.4	3.30	17.8	218	99.9	15.6	2.04	2.22	1.85
2006.9.08	20	2.81	2.48	86.4	10.9	54.8	25.9	98.0	99.8	3.54	5.93	2.04	0.93
2006.10.18	16	7.13	7.32	174	12.6	19.8	242	235	99.6	29.8	10.9	5.74	1.30
2006.11.14	10	5.18	5.65	129	10.6	106	63.7	244	99.7	3.14	24.6	11.7	3.52
2006.12.30	2	7.78	5.14	104	11.4	46.5	6.33	120	99.7	4.50	28.3	33.7	9.07
Average	13.6	6.63	7.11	126	14.6	46.1	71.2	170	99.7	11.3	14.4	11.1	3.33

^a Percent none sea salt (PNSS) values were calculated based on equations as follows: if Cl/Na equivalent ratio > 1.17, $\text{PNSS}\% = 100 - 100 \times (\text{SO}_4/\text{Na})_{\text{seawater}}/(\text{SO}_4/\text{Na})_{\text{sample}}$; if Cl/Na equivalent ratio < 1.17, $\text{PNSS}\% = 100 - 100 \times (\text{SO}_4/\text{Cl})_{\text{seawater}}/(\text{SO}_4/\text{Cl})_{\text{sample}}$. Equations modified from Zhang and Liu (2004).

^b Formic, acetic and oxalate acids data are from Xu et al. (2010). They are the average concentration of organic acid in August, September, October, November and December, respectively.

Table 3

Total acid-soluble concentrations (in pmol/kg) of rare earth elements in unfiltered rain water.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Gd/Nd) _{SN}	(Gd/Yb) _{SN}	ΣREE	D-ΣREE/A-ΣREE(%) ^a
20060410	961.8	1920	241.7	960.7	186.9	40.45	194.1	26.19	156.9	23.57	62.65	5.34	16.92	1.48	1.39	6.20	4799	84.6
20060424	520.4	821.5	109.0	406.4	73.59	15.61	82.36	11.22	66.73	10.59	32.03	4.32	25.43	3.72	1.39	1.75	2183	89.2
20060509	347.5	579.4	75.7	313.7	58.30	12.76	62.04	8.39	49.19	7.82	23.73	3.19	19.70	2.80	1.36	1.70	1564	26.0
20060513	1092	1208	148.7	561.7	85.67	18.52	91.97	11.28	64.36	10.00	30.54	3.49	19.53	2.42	1.13	2.55	3347	59.6
20060526	487.0	840.2	115.0	478.1	100.4	23.17	111.4	15.24	96.20	15.45	46.20	6.27	39.74	5.62	1.60	1.52	2380	61.9
20060622	1338	2163	278.8	1039	192.1	42.56	208.7	26.96	165.4	26.67	83.05	10.83	70.87	8.99	1.38	1.59	5656	90.4
20060707	400.0	463.5	54.13	204.7	34.99	7.92	36.20	4.45	25.2	4.11	13.45	1.58	9.26	1.33	1.21	2.11	1261	64.2
20060714	586.7	771.0	99.53	375.0	69.15	15.51	73.80	9.88	58.87	9.48	29.21	3.79	24.04	3.30	1.35	1.66	2129	96.2
20060716	448.3	466.3	55.96	205.6	35.92	8.47	39.42	5.51	34.37	5.85	18.76	2.50	15.81	2.23	1.32	1.35	1345	97.8
20060718	370.5	508.8	78.10	320.4	61.41	13.89	67.35	9.02	54.88	8.98	27.64	3.49	22.16	3.13	1.44	1.64	1550	88.5
20060730	553.1	835.3	91.64	305.5	52.07	10.42	56.24	7.53	45.69	7.20	22.36	2.95	17.69	2.49	1.26	1.72	2010	98.8
20060801	599.3	822.4	99.69	369.6	67.17	14.43	72.38	9.66	58.94	9.80	31.39	4.25	27.86	3.97	1.35	1.41	2191	63.4
20060806	219.9	425.1	48.58	208.6	46.04	12.44	43.97	6.31	35.99	6.29	21.76	2.94	18.00	2.77	1.45	1.32	1099	96.1
20060807	491.0	804.6	101.5	430.5	91.04	20.57	91.37	12.70	79.00	12.49	39.94	5.33	36.84	5.22	1.46	1.34	2222	58.9
20060822	345.3	605.1	87.0	275.3	53.28	11.51	53.06	7.51	45.06	7.11	23.01	3.21	20.66	2.78	1.32	1.39	1540	97.8
20060908	351.7	702.9	84.6	264.8	53.17	10.97	51.52	6.92	40.74	6.30	19.46	2.54	16.19	2.29	1.34	1.72	1614	74.7
20061008	959.1	1734	217.1	767.3	148.5	32.32	160.3	21.45	128.6	21.04	65.88	8.40	49.89	6.86	1.44	1.74	4320	93.2
20061018	908.6	1577	203.0	754.7	146.6	34.03	162.1	21.59	135.4	21.82	66.01	8.27	48.05	6.33	1.48	1.82	4093	96.4
20061114	1123	2171	293.0	1187	246.0	55.99	260.5	36.42	218.6	35.27	107.0	13.95	84.64	11.61	1.51	1.67	5845	83.5
20061230	532.1	925.2	106.3	395.1	70.67	15.47	83.24	11.63	71.69	12.04	38.43	5.15	33.05	4.58	1.45	1.36	2305	85.5

There is a lack of the sample (20060425) for total acid-soluble REEs analysis because the precipitation in that day weren't enough.

^a D-ΣREE/A-ΣREE(%) is ratio of total dissolved REE concentration to total acid-soluble REE concentration.

concentration in rainwater may be its acidity. The SO₂, NO_x and organic acids in the atmosphere could dissolve in clouds or water droplets, resulting in acidification of the original rainwater. When the mildly acidic rainwater encounters atmospheric particles, the REEs could be released to solution by either leaching from or dissolution of particles. This suggests that acidification of rain water is associated with enhanced release of REE from airborne particles. That also explains why total dissolved REE concentrations in rainwater from October to April are higher than those from May to September.

4.3. Speciation of the REEs in rainwater

Speciation calculations were performed for the five samples collected from Guiyang during the period from August to December. The formations of complexes of REEs with PO₄³⁻, CO₃²⁻ and HCO₃⁻ can be ignored because almost no PO₄³⁻, HCO₃⁻ and CO₃²⁻ can be detected in rainwater from Guiyang. Although we did not measure organic acids, organic acid data for rainwater from August to December 2006 obtained in a previous study (Xu et al., 2010) are used in our model. The formations of REE complexes with SO₄²⁻, NO₃⁻, Cl⁻, F⁻, HCOO⁻ (Formate), CH₃COO⁻ (Acetate, AC⁻), and C₂O₄²⁻ (Oxalate, Ox²⁻) were considered in the calculations, and the importance of Ln³⁺, LnSO₄⁺, LnOx⁺, LnOx₂⁻,

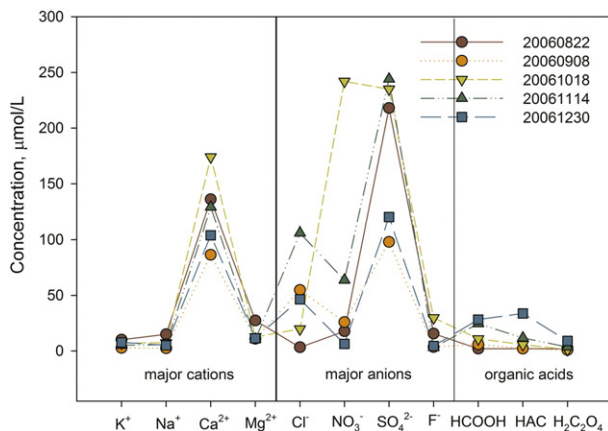


Fig. 2. Schoeller diagram of concentrations of major species in rainwater. Organic acids concentrations are from Xu et al., 2010.

LnOH²⁺, LnAC²⁺, LnF²⁺, LnCl²⁺, Ln(Formate)²⁺, and LnNO₃²⁺ species were evaluated.

The calculations reveal that the dominant species are the free metal ion species (Ln³⁺), sulfate complexes (LnSO₄⁺), oxalate complexes (LnOx⁺ and LnOx₂⁻) and fluoride complexes (LnF²⁺) in rainwater from Guiyang (Fig. 5a-e). All of the other REE complexes, including Ln(Acetate)²⁺, LnCl²⁺, Ln(Formate)²⁺, and LnNO₃²⁺ complexes, are negligible and account for <0.1% of each dissolved REE. For most rainwater samples, the free metal species is considered to be the primary form of the dissolved REEs and accounts for between 9.9% and 84.7% of the total REEs. The proportions of each REE presented as the free metal ion in rainwater decrease with increasing atomic number across the series. LnSO₄⁺ is the most important inorganic complex in solution, accounting for 0.8%–18.2% of dissolved REEs. Although the stability constants for REE-sulfate increase slightly with increasing atomic number from La to Eu (Fig. 6), the proportion of each REE complexed with

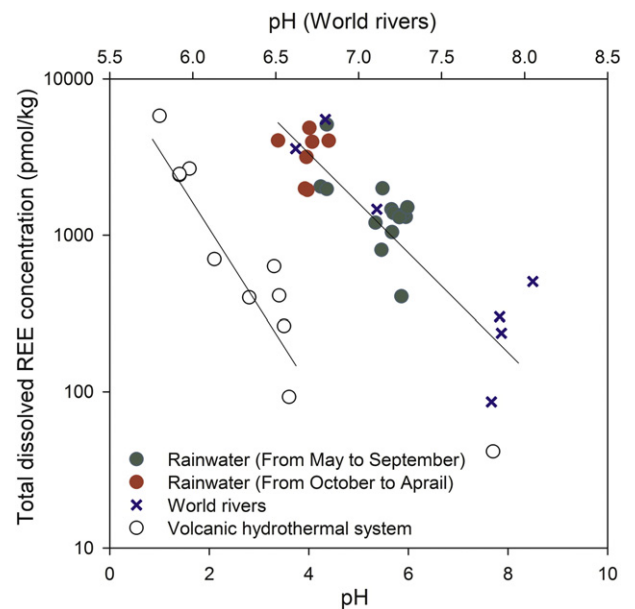


Fig. 3. Concentrations of the total dissolved REE versus pH for waters from Guiyang fallout events, the world's large rivers (Goldstein and Jacobsen, 1988a, 1988b) and volcanic hydrothermal systems (Inguaggiato et al., 2015).

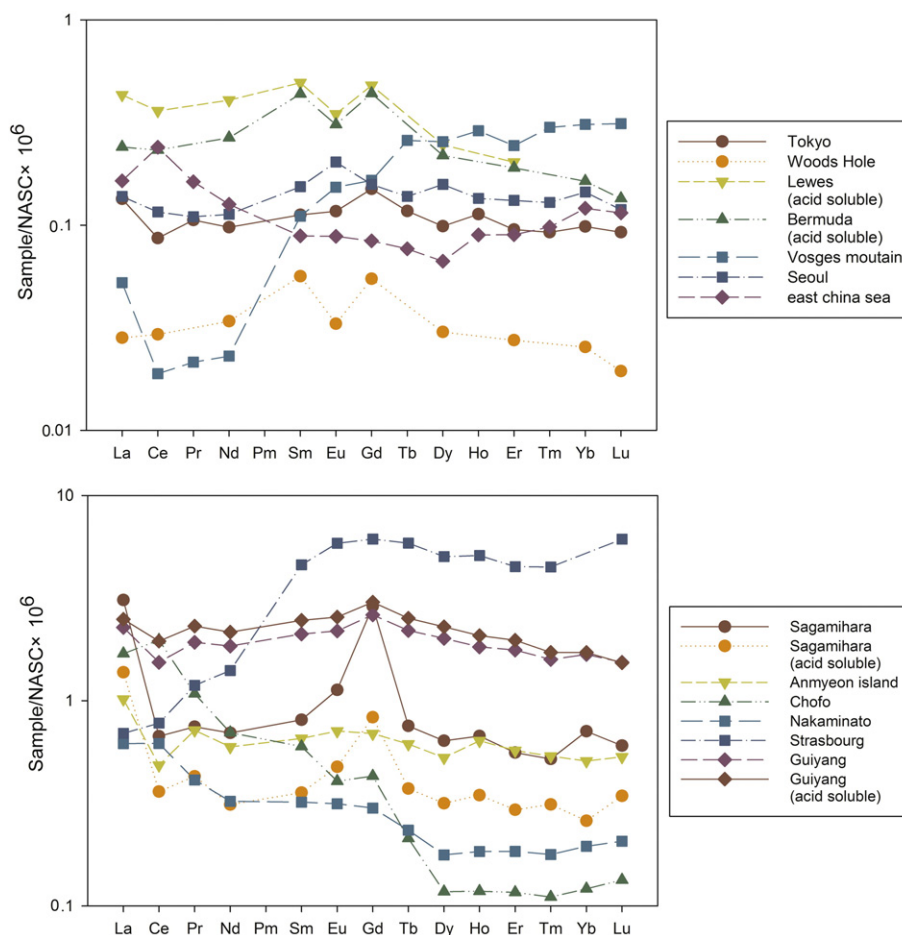


Fig. 4. REE abundances in rainwater normalized to shale (NASC). All the REEs data for shale-normalized are mean or unique value that from Aubert et al. (2002), Iwashita et al. (2011), Ryu et al. (2007), Shimamura et al. (2007), Sholkovitz et al. (1993), Soyol-Erdene et al. (2011) and Zhang and Liu (2004).

sulfate decreases or remains constant due to the effect of competition of the REE-oxalate complexes. The proportion of LnSO_4^+ accounting for dissolved metal distinctly decreases with atomic numbers larger than 63 (Gd) because the stability constants for LnSO_4^+ also markedly decrease with increasing atomic number from Gd to Lu (Fig. 6). LnF_2^+ is another common inorganic complex in rainwater from Guiyang, and its importance, similar to its stability constant, gradually increases with increasing atomic number. The stability constants show less difference for LnF_2^+ and LnSO_4^+ (Fig. 6). However, the F^- concentration is far lower than that of SO_4^{2-} in rainwater, and LnF_2^+ is of minor importance for the majority of the rainwater. LnF_2^+ complexes account for <10% of the total metal for each REE, even though the F^- concentration is as high as $29.8 \mu\text{mol/L}$ in the sample collected on October 18 (Fig. 5c). However, for this rainwater with a high F^- concentration, the HREE-fluoride complexes are sometimes more important than HREE-sulfate complexes in solution.

Unlike in surface water, the organic ligands in rainwater from Guiyang are mainly carboxylic acids. Formic acid, acetic acid and oxalic acid were found to be the predominant carboxylic acids (Xu et al., 2010). The stability constants for REE complexes with oxalate are approximately three orders of magnitude higher than for REE-formate and REE-acetate complexes (Fig. 6). Thus, REE-oxalate complexes are the most important organic complexes in rainwater from Guiyang (Fig. 5a–e). The REE-oxalate complexes (LnOx^+ and LnOx_2^-) account for 5.2%–69.9% of the dissolved REE. Monooxalate complexes (LnOx^+) and dioxalate complexes (LnOx_2^-) account for 5.1%–69.4% and 0.1%–19.4% of dissolved REE, respectively. Monooxalate complexes are considered to be more important than dioxalate complexes in rainwater collected in Guiyang. The proportions of LnOx^+ and LnOx_2^- increase

with increasing atomic number across the entire REE series. For the rainwater collected on October 18 (Fig. 5c), the ratio of oxalic acid to sulfate is approximately 1:180 and the proportion of LREE-sulfate complexes accounting for dissolved REEs is higher than that of LREE-oxalate complexes, but that of HREE-oxalate complexes is higher than that of HREE-sulfate complexes. For the rainwater collected on September 8 (Fig. 5b), the ratio of oxalic acid to sulfate is approximately 1:105 and the proportion of all of the REE (except La and Ce) complexes with oxalate is higher than that of REE-sulfate complexes. For the rainwater collected on the December 30 (Fig. 5e), the ratio of oxalic acid to sulfate is approximately 1:13, the LnSO_4^+ species is of minor significance in solution, accounting for <8% of the total metal for each REE. The free metal ions and REE-oxalate species are the dominant species of dissolved REEs. Approximately 81.4% of total anions were dominated by SO_4^{2-} , with oxalate accounting for 1.0% of the total anions in rainwater from Guiyang (Xu et al., 2010). Because oxalic acid is a weak acid, the ratio of oxalic acid to sulfate that complexes with REEs is far higher than 1.0:81.4. This indicates that the proportion of REE complexes with oxalate accounting for dissolved REEs is higher than that of REE complexes with sulfate in the rainwater from Guiyang.

The contribution of oxalic acid to free acidity in some rain events was up to 80% in Guiyang (Xu et al., 2010). Although rainwater samples with high concentrations of oxalic acid were not collected, the REE complexation behavior can also be predicted by adjusting the concentrations of oxalic acid and sulfate in PHREEQC. Because the stability constants for REE-chloride and REE-nitrate complexes are far lower than those for REE-oxalate and REE-sulfate (Fig. 6), the complexation reaction between REEs with chloride and nitrate can be ignored. This prediction is based on the assumption that the oxalic acid concentrations are 30,

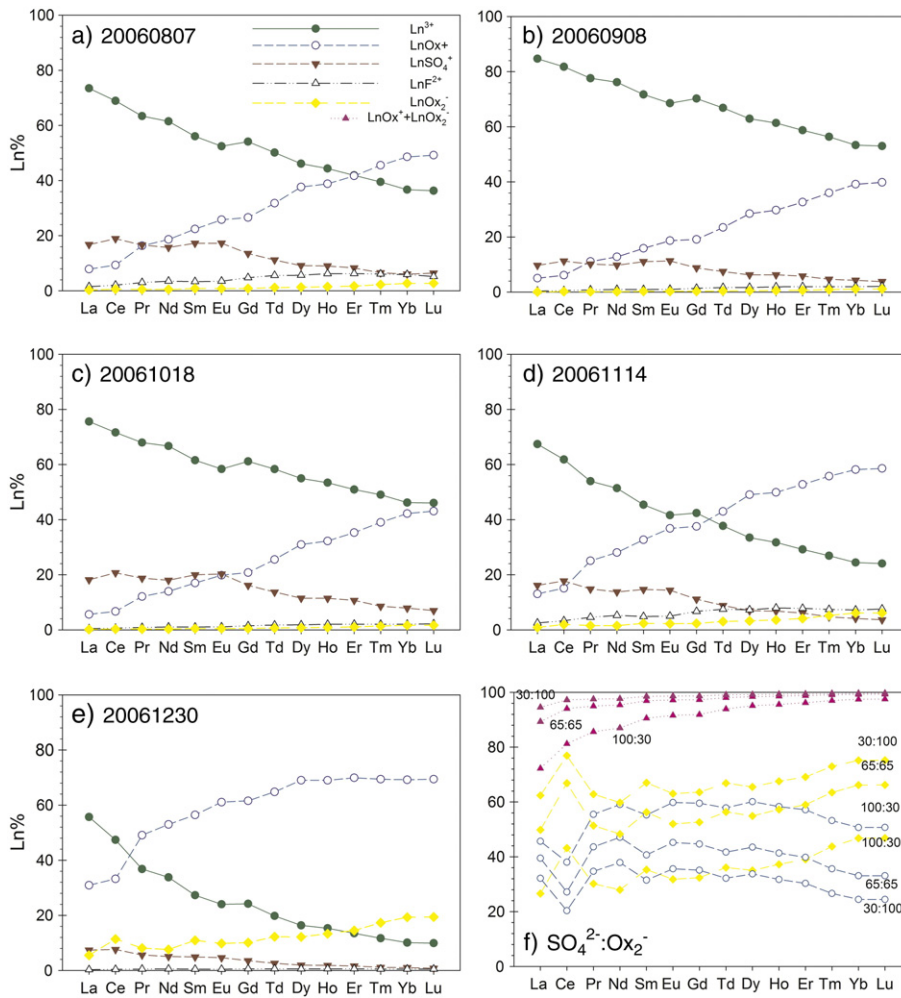


Fig. 5. Results of speciation modeling plotted as percent dissolved rare earths (i.e. %Ln) vs. atomic number for rainwater samples from Guiyang: (a) 20060807, (b) 20060908, (c) 20061018, (d) 20061114, (e) 20061230 and (f) the assumed ratio of sulfate to oxalic acid for predict REE complexation behavior in rainwater where oxalic acid have an important contribution to the acidification of the rainwater.

65, and 100 μmol/kg and the sulfate concentrations are 100, 65, and 30 μmol/kg, respectively (Fig. 5f). All of the other physical and chemical parameters are based on the parameters of rainwater collected on

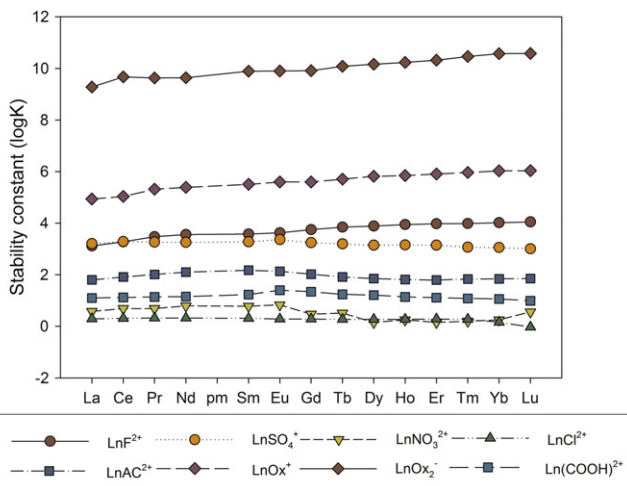


Fig. 6. The stability constants (LogK) for REE complexes with Fromate and Acetate acids (25 °C, I = 0.1 mol/kg), Oxalate acid (25 °C, I = 0.05 mol/kg) and inorganic ions (25 °C, I = 0 mol/kg). Data for LogK are from Martell et al. (2004), Schijf and Byrne (2001) and Millero (1992), respectively. Here, I denote ionic strength.

December 30. When the ratio of oxalic acid to sulfate is 30:100, LnOx⁺ and LnOx₂⁻ species are dominant in the acid rain. LREE (La,Ce,Pr,Nd)-oxalate complexes account for 72%–87% of the dissolved REEs, whereas the other REE-oxalate complexes account for 91%–98% of the dissolved REEs. The proportion of LnOx⁺ is higher than that of LnOx₂⁻ in solution. When the concentration of oxalic acid and sulfate became equal, the proportion of LnOx₂⁻ became higher than that of LnOx⁺. When the ratio of oxalic acid to sulfate is 100:30, almost all of the REEs bound to oxalate in solution and REE-oxalate complexes account for >95% of the dissolved REEs. The proportion of LnOx₂⁻ accounting for dissolved REE is approximately 2–3 times higher than that of LnOx⁺. The proportion of LnOx₂⁻ accounting for dissolved metals increases with increasing oxalic acid concentrations. On the contrary, the proportion of LnOx⁺ accounting for dissolved metals decreases with increasing oxalic acid concentrations. The proportion of LnOx₂⁻ (except CeOx₂⁻) significantly increases with increasing atomic number, whereas the proportion of monoxalate complexes (except CeOx⁺) for the MREE is higher than for the LREE and HREE in solution.

The stability constants for LnOx⁺ and LnOx₂⁻ are similar to those of LnCO₃⁺ and Ln(CO₃)₂⁻ and gradually increase with increasing atomic number across the entire lanthanide series. If the shale-normalized REE patterns for the rainwater (such as rainwater from Strasbourg and Vosges) exhibit HREE enrichment, the complexation of REEs and oxalate should be considered. This may be caused by the formation of stable oxalate complexes in solution where the HREE preferentially form stronger oxalate complexes than the LREE.

4.4. Shale-normalized REE patterns

4.4.1. Anthropogenic positive anomaly of La

In shale-normalized REE of natural water or rocks, the elements from La to Lu commonly form one coherent group. However, in some cases, Ce and Eu behave anomalously with respect to their neighboring REEs. The deviation of Ce and Eu is usually defined as the Ce and Eu anomaly. Following previous studies (Debaar et al., 1985; Alibo and Nozaki, 1999; Kulakosz and Bau, 2013), the La anomaly in this work can be denoted as

$$\text{La/La}^* = \text{La}_{\text{SN}} / \left(3 \text{Pr}_{\text{SN}} - 2 \text{Nd}_{\text{SN}} \right) \quad (1)$$

where the subscript SN denotes normalization to shale (North American shale composite, NASC) and the superscript * denotes the geogenic background (extrapolated). Thus, a positive or negative anomaly is defined as a La/La* value greater or less than unity, respectively.

Most of the rainwater samples (dissolved fractions) collected from Guiyang show La anomalies, ranging from 0.68 to 2.32 with an average of 1.25 (Fig. 7, and Table 1). A La anomaly is also exists in acid-soluble fractions, ranging from 0.67 to 1.64 with an average of 1.23. A positive La anomaly was commonly detected in rainwater in Japan and lake waters in Guiyang (Iwashita et al., 2011; Shimamura et al., 2007; Wang et al., 2013). In particular, the value of La/La* obtained for rainwater collected from suburban Tokyo was as high as 3.65 (Iwashita et al., 2011). The zeolite cracking catalysts used for petroleum refining are considered a primary anthropogenic La source for rainwater because these are strongly enriched in light REEs (Olmez and Gordon, 1985; Olmez et al., 1991; Kitto et al., 1992; Kulkarni et al., 2006, 2007; Censi et al., 2011). However, the value of La/La* for the cracking catalysts, which was calculated according to the data provided by Kulkarni et al. (2006), was only 1.06. Moreover, Guiyang City lies in the center of Guizhou Province, in an area of approximately $1.67 \times 10^5 \text{ km}^2$ without oil refineries. Thus, the zeolite cracking catalysts used for petroleum refining might not be an important source of La for rainwater in Guiyang.

The values of La/La* were 1.08, 0.53 and 0.90 in Chinese loess, local soil and the upper crust, respectively (Taylor and McLennan, 1985; Yokoo et al., 2004; Chen and Yang, 2010). These values are significantly lower than the La/La* values of most rain events. This suggests that terrigenous deposits are not the source of positive La anomalies. La-rich

carbonates are employed as catalytic converters during hydrocarbon combustion in power stations (Censi et al., 2011). That is also a possible anthropogenic La source in rainwater. However, China is a major coal-producing country, and coal is mainly consumed in the domestic energy sector. A major cause of acid rain in Guiyang is presumably the extensive use of coal (Xiao and Liu, 2004). Coal is the sole energy source for electricity generation in coal-fired power plants in Guiyang. The mean value of La/La* in coal used in local plants is only 0.90 (Zhang et al., 2010); hence, it is obvious that coal and La-rich carbonate cannot produce La anomalies. The $(\text{La/Ce})_{\text{SN}}$ and La/La* for the automobile catalyst SRM 2556 were 1.60 and 1.61, respectively (Fig. 7) (Kulkarni et al., 2006). The automobile catalyst seems to be an important source of anthropogenic La in rain. However, the shale-normalized ratio of La to Sm was up to 35.7, which is far higher than that of rainwater from Guiyang (Fig. 7). Therefore, the automobile catalyst could not be the main anthropogenic source of La in rainwater. The REE compositions of inhalable particulate matter (PM2.5) in the tunnel can indicate the REE compositions of emissions from automobiles. The value of La/La* was 13.6 in PM2.5 collected in the Washburn tunnel (Fig. 7) (Kulkarni et al., 2006). This illustrates that emissions from automobiles might be representative of an obvious positive La anomaly. Thus, automobile emissions may be an important source of anthropogenic La. However, the value of the $(\text{La/Ce})_{\text{SN}}$ of automobile emissions was only 0.46 (Fig. 7), which is less than that in the rainwater samples, and thus, an additional source of anthropogenic La must exist for the rainwater in Guiyang.

In East Asia, especially in China, REE fertilizer has been widely used since the 1990s. Approximately $1.3 \times 10^6 \text{ kg}$ of REEs is consumed on agricultural land every year (Pang et al., 2002; Wang et al., 2008). There are basically three types of REE fertilizers in China: Changle-Yizhisu (CY), which contains nitrate forms of REEs; Nongle, which contains chloride forms of REEs; and MAR (REE complexes of mixed amino-acids), which contains 17 types of amino-acids together with La, Ce, Pr and Nd. The three types of fertilizers are similar in terms of REE composition. At present, CY is used by most local farmers in China. In CY, the La concentration is 174.2 g/Kg, La/La* is 1.73, and $(\text{La/Ce})_{\text{SN}}$ is 8.38 (Wang et al., 2004). In China, there are mainly two ways to use REE fertilizers (Liu et al., 1997; Wang et al., 2004). The first is foliage dressing, in which REE fertilizer is sprayed through leaves in the jointing stage of spring planting. The total amount of La input in the foliage dressing field is 107 g/hm^2 each year. The total output of La from plants and

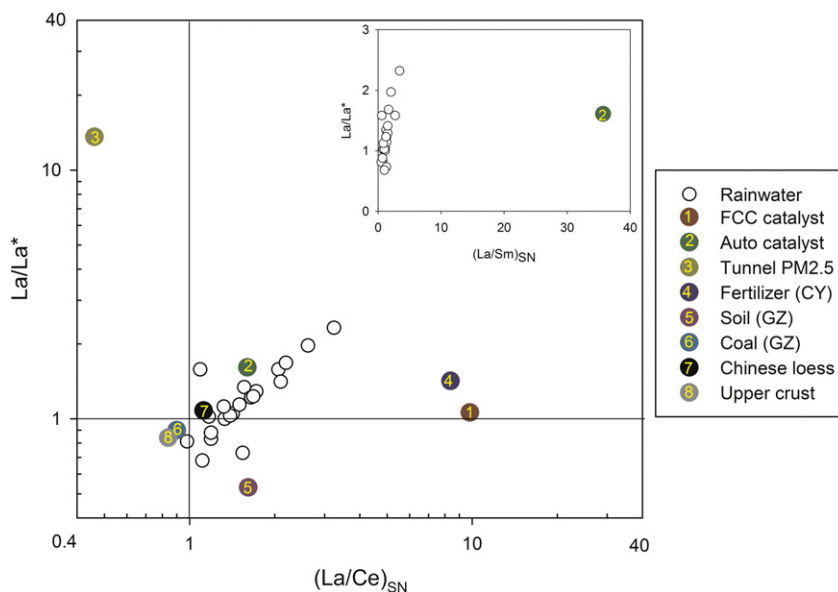


Fig. 7. $(\text{La/Ce})_{\text{SN}}$ and La/La* in Rainwaters (Guiyang), FCC catalyst, Auto catalyst, Washburn tunnel (Kulkarni et al., 2006), Fertilizer (CY) (Wang et al., 2004), Soil(GZ) (Chen and Yang, 2010), Coal (GZ) (Zhang et al., 2010), Chinese loess (Yokoo et al., 2004) and Upper crust (Taylor and McLennan, 1985). The values of $(\text{La/Ce})_{\text{SN}}$ and La/La* are calculated from original data.

infiltrated water is only approximately 5 g/hm² each year. The amount of accumulated La in the field is therefore approximately 102 g/hm² each year when REE fertilizers are used in the foliage dressing field. The second method is soil dressing, in which REE fertilizer is directly used in soil with other fertilizers. The total La input in soil dressing is approximately 1176 g/hm² each year. The total La output in the soil dressing field is the same as in the foliage dressing field. Thus, the accumulated La in the field is approximately 1171 g/hm² each year (Wang et al., 2004). Regardless of the fertilization method, most of the La in REE fertilizers will accumulate in the surface soil of the agricultural field. When these soil particles are released into the atmosphere, the positive La anomaly in rainwater is promoted. This suggests that REE fertilization is another important source for the positive La anomaly.

4.4.2. Shale-normalized REE patterns in rainwater

In the case of acidic or mildly acidic terrestrial waters, shale-normalized middle REE (MREE) enrichments have been commonly reported (Elderfield et al., 1990; Johannesson and Lyons, 1995; Sholkovitz, 1995; Hannigan and Sholkovitz, 2001; Johannesson et al., 2004). Shale-normalized REE patterns for rainwater (dissolved fractions and acid-soluble fractions) from Guiyang are also enriched in the MREE

compared to LREE and HREE (Fig. 8a-b). The mean values of (Gd/Nd)_{SN} and (Gd/Yb)_{SN} are respectively 1.39 and 1.58 in dissolved fractions, and respectively 1.38 and 1.88 in acid-soluble fractions. Shale-normalized REE patterns of emissions by car are not illustrated in Fig. 8c because concentrations of MREE and HREE in tunnel PM2.5 were lower than detection limits (Kulkarni et al., 2006). The MREE enrichment was not found in REE-fertilizer, Chinese loess, soil (from Guizhou, GZ) and coal (GZ) that were considered as possible important sources of aerosols particles (Fig. 8c) (Xiao and Liu, 2004; Xiao et al., 2010; Han et al., 2011). The REEs in rainwater are mainly derived from the washout or dissolution of aerosolparticles, and therefore, the MREE enrichment of rainwater could be the result of the interaction of water and airborne particles. There are two mechanisms to explain MREE enrichment in terrestrial water. One mechanism is solution complexation in water. The infinite-dilution stability constants for MREE complexes with sulfate, nitrate, fromate, acetate and humic acid are higher than the stability constants for the formation of the same complexes with LREE and HREE (Fig. 6) (Millero, 1992; Martell et al., 2004). In the absence of other geochemical processes, this solution complexation may contribute to the MREE enrichment. In fact, the stability constants for REE-nitrate, REE-fromate and REE-acetate are too small for the complexation

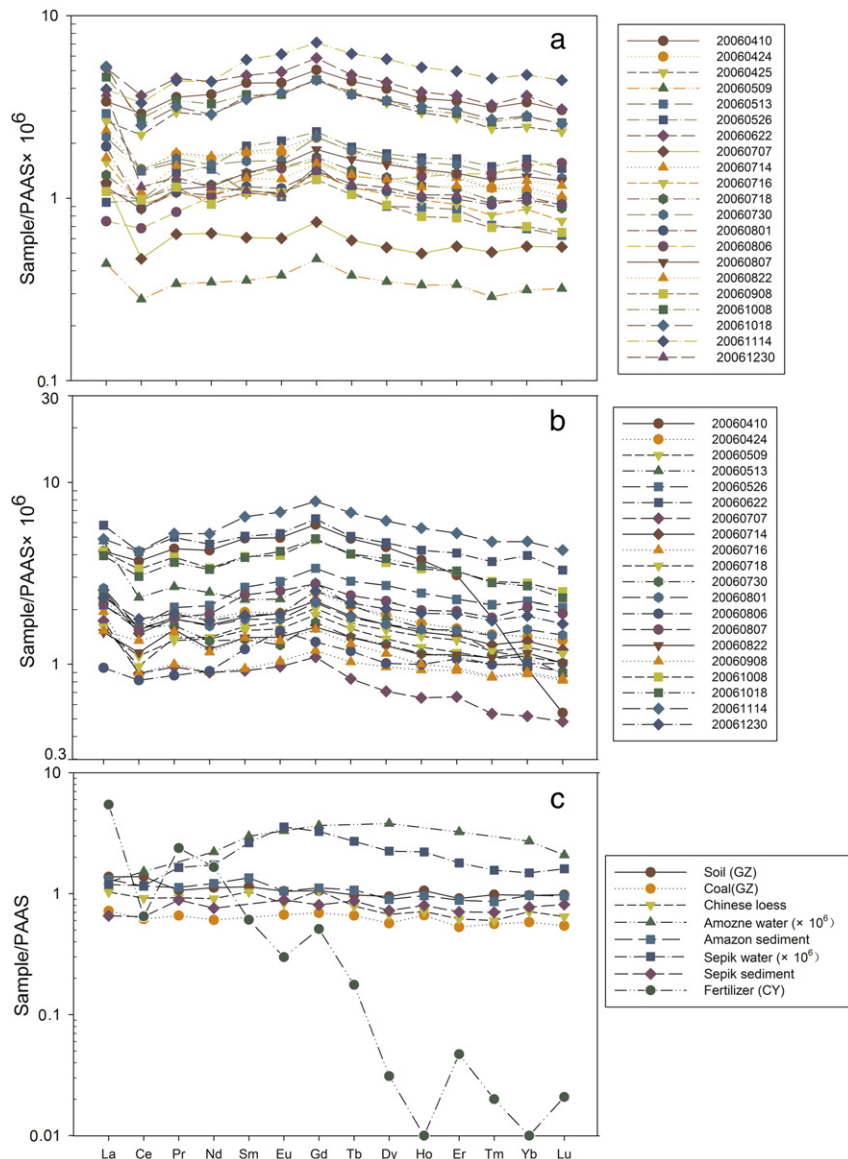


Fig. 8. Patterns of shale-normalized REEs. (a) Dissolved REEs in rainwater from Guiyang. (b) Acid-soluble REEs in rainwater from Guiyang. (c) Possible end-members of atmospheric particles in Guiyang and rivers sample from Amazon and Sepik (Hannigan and Sholkovitz, 2001).

reactions between REEs and the three ligands and can be neglected in the rainwater from Guiyang. There is almost no humic acid in rainwater, suggesting that the complexation of REEs with humic acid does not play a role in enriching MREE in rainwater. SO_4^{2-} is the most important anion in rainwater from Guiyang. However, according to the speciation calculation, even if the SO_4^{2-} concentration is up to 240 $\mu\text{mol/L}$ in rainwater samples, the LnSO_4^+ complexes still account only for <20% of the total metal for each REE (Fig. 5d). REE-sulfate complexes may exert little control on the development of the MREE-enrichment patterns. From the above discussion, it is clear that complexation does not lead to MREE-enrichment in rainwater.

The other mechanism of MREE enrichment is dissolution or leaching occurring on the surfaces of particles. Hannigan and Sholkovitz (2001) showed that leaching solutions derived from various river sediments at different pH levels were all enriched in MREE. Acidic water can dissolve carbonate minerals and most phosphatic minerals and desorb the adsorbed REEs from particle surfaces. These starting sediments show no MREE enrichment in spite of MREE enrichment in the river waters (Fig. 8c). The dominant crustal rocks (sandstone, shale, granite) and rock-forming minerals (quartz, xenotime, olivine, pyrite, monazite, plagioclase, and clay minerals) also do not show MREE enrichment (Taylor and McLennan, 1985). The absorption-desorption reactions associated with changes in pH cannot be responsible for the MREE enrichment in solutions (Sholkovitz, 1995). In contrast, the REE compositions of many phosphatic minerals show well-developed MREE enrichment. They demonstrate that the weathering of phosphate minerals can result in MREE enrichment. One of the three largest phosphate mines in China is located in Guiyang (Xiao and Liu, 2004). It contains >70% of the high-quality phosphate ore in China. Phosphatic minerals can be released into the atmosphere easily during ore mining and processing. It is conceivable that leaching and/or dissolution of phosphatic minerals in airborne particle can lead to MREE enrichment in rainwater. Byrne et al. (1996) illustrated that the precipitation of phosphates from solution results in the preferential removal of dissolved MREE and the formation of MREE-enriched precipitates. It is also possible that a similar process generated the MREE enrichment in the surface soil of Guiyang. In the rain events or irrigation, the MREE-phosphate complexes are preferentially retained at the surface of soil particles on the topsoil and the LREE- and HREE-complexes associated with water are removed to deeper soil. The topsoil particles enriched in MREE phosphate complexes might also be a source of airborne particles, contributing to the development of the MREE enrichment fractionation patterns of the rainwater.

As mentioned above, HREE enrichment has been commonly reported in water with high carbonate and CO_2 concentrations. It is interesting that CO_2 -rich waters (pH = 9) from the top and bottom of 'Specchio di Venere' Lake also enrich in MREE (Inguaggiato et al., 2016). The REE pattern of lake water was similar to a desert varnish of Saharan origin, consisting mainly Fe- and Mn-oxyhydroxide coatings and clay minerals. Greaves et al. (1994) carried out a dissolution experiment of the desert varnish with seawater and found that MREE had a higher solubility than LREE and HREE. MREE enrichment was also observed in hydroxylamine hydrochloride-acetic acid, which was used to react with some crushed rock samples from Canada (Johannesson and Zhou, 1999). The leachates mainly contained REEs associated with Fe-Mn oxide/oxyhydroxide cements and/or mineral/amorphous phases. Consequently, MREE enriched Fe-Mn oxides/oxyhydroxides could be another pathway for enriching MREE in rainwater.

5. Conclusions

The concentrations of total dissolved and acid-soluble REEs in rainwater from Guiyang of Southwest China are higher than those in most of the world's cities (except for MREE and HREE in Vosges) and local surface water. The pH of rainwater from May to August is higher than in other months, but the concentrations of dissolved REEs in rainwater from May to August are lower than in other months in the same year.

The dissolved REE concentrations are negatively correlated with pH, indicating that acidification of rainwater could result in an increase in concentration of REEs in rainwater. Speciation calculations predict that the free REE metal ions (i.e., Ln^{3+}), sulfate (LnSO_4^+), oxalate (LnOx^+ and LnOx_2^-) and fluoride (LnF_2^+) complexes are important forms of dissolved REEs. All of the other REE-complexes are negligible. Although the contribution of oxalic acid to rain water acidity is much less than sulfate acid, most of the REEs complexes with oxalate are more important than REE-sulfate complexes in rain events. With increasing oxalic acid concentration, the REE complexes with oxalate instead of free metal ions become the dominant species. Complexation of REEs with oxalate can play an important role in HREE enrichment in solutions because stability constants for REE-oxalate complexes gradually increase from LREE to HREE. Shale-normalized REE patterns for rainwater also show enrichment in MREE compared to LREE and HREE. The original raindrops dissolve and/or leach MREE-enriched airborne particles, likely controlling the development of MREE enrichment in rainwater. Despite the fact that SO_4^{2-} is the most abundant anion in rainwater, REE-sulfate complexes may exert little control on the development of the MREE-enrichment patterns. In the shale-normalized REE pattern plot, La shows a clear positive anomaly in most of rainwater. The local soil, coal and Chinese loess cannot be important sources of excess La because their values of La/La^* are relatively low. The La anomaly might derive from two important sources. The first is La from automobile emission; the second is REE-fertilizer that has been widely used in the agriculture of China.

Acknowledgements

We thank Dr. Carla M. Koretsky very much for handling the editorial functions and improving the final version of this manuscript. We also thank Dr. Peter Möller and an anonymous reviewer for constructive comments that improved the quality and the clarity of the manuscript. This work was jointly supported by the National Science Foundation of China under the projects 41673026, 41372373, 31270510, and the Natural Science Foundation of Tianjin under the project 14JCYBJC22400.

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