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

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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.

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 Sagamihara (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 km^2 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.,

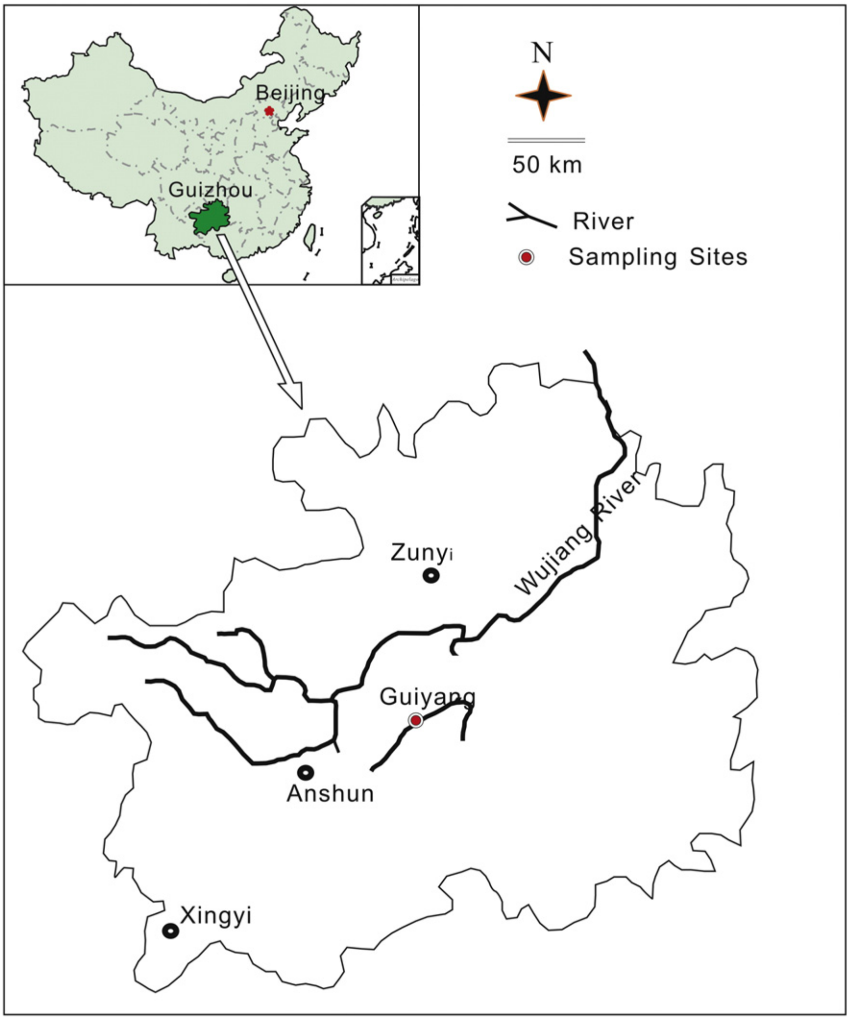

Fig. 1. Simplified map of sampling location.