

## Rare earth element geochemistry of waters and suspended particles in alkaline lakes using extraction and sequential chemical methods

ZHONG-LIANG WANG,<sup>1,2\*</sup> CONG-QIANG LIU<sup>2</sup> and ZHAO-ZHOU ZHU<sup>1</sup>

<sup>1</sup>Tianjin Key Laboratory of Water Resources and Environment, Tianjin Normal University, Tianjin 300387, China

<sup>2</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

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The concentrations of rare earth elements in the waters and suspended particles from two alkaline lakes in a carbonate drainage basin of the South China Karst region were determined via ICP-MS. Sequential chemical extraction experiments were conducted on the suspended matter to investigate water-particle interaction processes. Due to their high pH, the alkaline lakes have lower concentrations of dissolved rare earth elements than those reported for most other terrestrial surface waters of the world. Linear regressions between pH and the rare earth element (REE) concentrations over a wide pH range show a “three stage model,” implying the geochemical behavior of dissolved REEs in surface waters is mainly controlled by pH. Shale-normalized patterns of dissolved REEs mainly show a marked enrichment in heavy REEs (HREE), while acid-extracted and organic REEs mainly show convex patterns and the residual fractions have flat patterns. Distinct positive La anomalies were observed in the Lake Aha and its river waters, which also exhibit a very high Mn concentration, indicating severe redox and scavenging conditions. Both negative and positive Ce anomalies were clearly observed in the dissolved phase and extracted fractions of suspended particulate matter. The positive correlation of Ce anomalies with Mn indicates that redox reactions control these Ce anomalies.

Keywords: rare earth elements, alkaline lake, dissolved, suspended particles, sequential chemical extractions

### INTRODUCTION

The rare earth elements are an extremely coherent group in terms of chemical behavior and have been widely used as tracers of various geochemical processes in terrestrial water systems (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990; Byrne and Lee, 1993; Zhang and Liu, 2004; Lawrence and Kamber, 2006). However, changes in pH, redox conditions, and adsorption/desorption reactions in aqueous systems easily fractionate REEs through formation of solution and surface complexes, cation exchange reactions, and transport by colloids (Byrne and Kim, 1990; Wood, 1990; Gosselin *et al.*, 1992; Tanizaki *et al.*, 1992; Koepfenkastro and De Carlo, 1993). Thus, suspended particulate matter (SPM) plays an important role as a phase of REE migration within the hydrological cycle. The labile fractions, such as cation-exchangeable, adsorbed and Fe–Mn oxide fractions of SPM are especially sensitive to REEs and important to REE fractionation. Geochemical analysis of REE solid

speciation by sequential chemical extraction is important and necessary for REE research in surface waters (Yan *et al.*, 1999).

Many geochemical studies of REEs in rivers, estuaries, and oceans have been conducted and there is a wide range of REE data within the aquatic chemistry literature. However, the fundamental REE geochemistry of lakes is poorly documented (Elderfield *et al.*, 1990; Sholkovitz, 1993). Lakes are complex and dynamic biogeochemical, chemical, and physical systems that differ from rivers and oceans. Due to seasonal stratification and redox condition shifts, material exchange processes frequently occur between water, SPM, and bottom sediments in lake systems. These processes can markedly affect the chemical processes involving REEs in lake waters. Our knowledge of REE concentration and their fractionation behavior in terrestrial alkaline lakes is particularly limited, with few alkaline lakes having been investigated in this context (Johannesson and Lyons, 1994). One reason for this is the difficulties involving in analyzing the very low concentrations of dissolved REEs present in alkaline lakes. However, these lakes provide a useful opportunity to investigate and improve understandings of the mechanism of REE fractionation and behaviors in the aquatic systems. Many alkaline lakes

\*Corresponding author (e-mail: wangzhongliang@vip.skleg.cn)

have complicated geochemical characters, owing to their different geographic settings, the influences of various water and/or particulate matter sources, and also the possible impact of human activities.

The main purposes to be addressed in the present study are: (1) to elucidate the geochemical processes that determined the abundance of the REEs; and (2) to investigate the fractionation behavior of REEs in two typical alkaline lakes located at the South China Karst area.

## SAMPLING AND ANALYSIS

### *Geographic background of the lakes*

Maps of Lake Hongfeng and Lake Aha and the sampling locations are presented in Fig. 1. The two lakes are located in the center of the Guizhou Province, in the South China Karst region. Lake Hongfeng is ~16 km long with a maximum width of 4 km. The surface area is ~57.3 km<sup>2</sup> and the total water volume is ~3 × 10<sup>8</sup> m<sup>3</sup>. Permian and Triassic carbonates are the predominant bedrock types within the Lake Hongfeng drainage basin. Lake Aha is smaller than Lake Hongfeng, with a surface area of 3.4 km<sup>2</sup> and a total water volume of ~4.45 × 10<sup>7</sup> m<sup>3</sup>. The Lake Aha drainage basin bedrock consists mainly of Permian carbonates. Since the two lakes both flow through carbonate catchments, they are typically alkaline lakes.

### *Sampling and analytical procedure*

Water samples were taken by a 5-L sampler at distinct depths in the water profiles from Lake Hongfeng (H1 and H2) and Lake Aha (A1 and A2) in January 7–9, 2001. Samples of river water sample from their inflowing tributaries were also collected (HRs and AR). pH, temperature, and dissolved oxygen (DO) were measured *in situ*. Water samples for determining dissolved REEs were filtered immediately using 0.22 μm Millipore membrane filter and stored in 2 L high-density polyethylene bottles and acidified with ultra-purified hydrochloric acid until pH < 1.5 to prevent adsorption and microbial activity during storage. The residual solids retained on the membrane were also collected. These were dried in an oven at ~60°C then weighed to determine the concentration of SPM.

When transferred into the laboratory, preconcentration by a factor of at least 200 and purification of dissolved REEs were performed by solvent extraction and back extraction procedures described by Shabani *et al.* (1990) and Zhang *et al.* (1994). REE concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, ELEMENT). The entire procedure was accomplished in a Class-100 laboratory. 18.2 MΩ Milli-Q water and high-purity reagents were used. Reagents and procedural blanks were also determined in parallel to the sample treatment. The ICP-MS operating parameters were

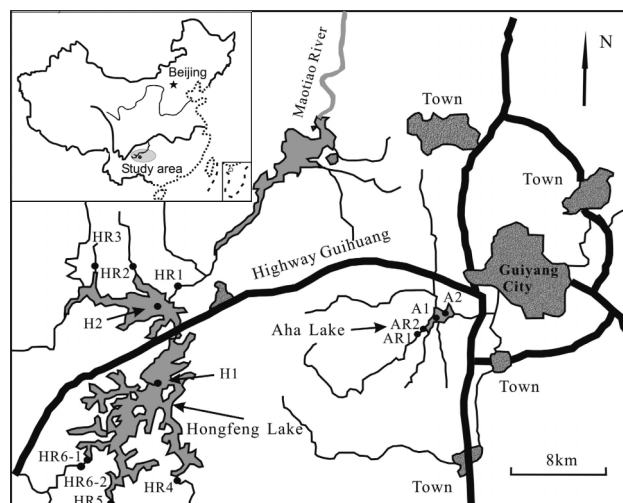


Fig. 1. Hongfeng Lake and Aha Lake and their inflow tributaries showing sampling stations.

set as follows: R.F. Power, 1350 w; Plasma gas, 14 L min<sup>-1</sup>; Auxiliary gas, 1.0 L min<sup>-1</sup>; Nebulizer gas, 0.84 L min<sup>-1</sup>. The following isotopes of REE were monitored during the ICP-MS measurement in order to minimize isobaric interferences: <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>153</sup>Eu, <sup>158</sup>Gd, <sup>159</sup>Tb, <sup>164</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>174</sup>Yb, and <sup>175</sup>Lu. The procedural blanks were 6% for La, 8% for Ce, and 3–5% for other REEs when compared to the lowest REE sample concentration. Accuracy of ±2.0% for each REE was evaluated by analysis of standard solutions provided by SPEX Industries, Inc. The precision of ICP-MS determination for REEs were better than ±3% for heavy REE and ±5% for light REEs of all samples (*n* = 156), with the exception of two samples (A1-1 and A2-5) which had a light REE precision of ~±12%.

Major anions and cations were measured using an Ion Chromatograph (DIONEX ICS-90), and an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Visata MPX), respectively, after acidification with ultra-purified nitric acid. The precision for major ions was better than ±2%. Dissolved Fe and Mn were determined by ICP-MS with a precision of ~±5% for Fe and ±2% for Mn.

REEs within the SPM can be classified into a labile fraction and residual (virtually insoluble) REEs. Numerous sequential extraction methods have been used to examine the various SPM phases using several different chemical reagents (Tessier *et al.*, 1979; Sholkovitz *et al.*, 1994; Négrel *et al.*, 2000). In the absence of an established sequential extraction method that targets REEs, we used the “continuous fractionation procedure” for REEs, modified from the method of Tessier *et al.* (1979). In this method, trace metals in the exchangeable, bound to car-

Table 1. The percent of REEs in different fractions in the Aha and the Hongfeng lakes and their river waters

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
AH1 <sub>dissolved</sub>	14.9	4.86	9.10	11.2	14.2	17.6	18.8	22.4	25.7	28.2	33.1	34.9	38.3	41.7
AH2 <sub>dissolved</sub>	16.1	2.11	8.14	11.4	17.3	19.8	21.7	27.0	30.0	33.1	38.7	43.3	48.0	53.1
AR <sub>dissolved</sub>	1.58	0.29	0.43	0.62	1.14	1.43	1.19	1.14	1.03	0.91	0.93	1.06	1.03	1.10
average	10.9	2.42	5.89	7.74	10.9	13.0	13.9	16.9	18.9	20.7	24.2	26.4	29.1	32.0
AH1 <sub>acid-extracted</sub>	45.5	40.9	48.6	49.8	46.6	47.7	46.3	41.2	38.3	35.4	29.8	26.2	22.0	18.8
AH2 <sub>acid-extracted</sub>	47.8	36.9	47.7	47.0	42.5	45.2	40.9	36.8	33.1	29.7	25.1	21.7	16.1	13.1
AR <sub>acid-extracted</sub>	50.9	40.2	55.1	58.6	60.2	61.2	60.1	58.2	54.4	52.6	48.0	44.2	39.3	38.8
average	48.1	39.3	50.5	51.8	49.8	51.4	49.1	45.4	41.9	39.2	34.3	30.7	25.8	23.5
AH1 <sub>organic</sub>	4.81	11.7	7.94	8.20	10.2	9.65	9.86	8.51	7.61	6.04	5.81	5.22	5.00	4.79
AH2 <sub>organic</sub>	8.07	20.6	12.2	13.1	16.6	13.4	16.7	12.9	13.0	11.9	10.2	9.42	8.51	7.38
AR <sub>organic</sub>	8.00	14.8	9.98	10.3	11.9	12.4	12.6	11.3	10.6	10.6	10.2	10.9	9.29	9.01
average	6.96	15.7	10.0	10.5	12.9	11.8	13.0	10.9	10.4	9.53	8.73	8.51	7.60	7.06
AH1 <sub>residual</sub>	34.7	42.5	34.4	30.8	29.0	25.0	25.0	27.9	28.5	30.3	31.3	33.7	34.8	34.8
AH2 <sub>residual</sub>	28.0	40.5	32.0	28.5	23.6	21.6	20.7	23.4	23.9	25.4	26.1	25.6	27.4	26.5
AR <sub>residual</sub>	39.6	44.7	34.5	30.5	26.8	24.9	26.2	29.4	34.1	35.9	40.8	43.8	50.4	51.1
average	34.1	42.6	33.6	30.0	26.4	23.9	24.0	26.9	28.8	30.5	32.7	34.4	37.5	37.5
H1 <sub>dissolved</sub>	16.4	7.70	15.0	18.2	21.5	23.4	23.3	26.8	28.9	33.4	36.1	39.2	43.1	48.4
H2 <sub>dissolved</sub>	26.4	9.18	23.1	26.8	31.5	34.0	35.2	39.5	41.4	43.7	47.1	49.3	52.0	57.1
HR <sub>dissolved</sub>	11.4	3.37	9.80	11.8	14.6	16.3	17.7	20.0	22.8	23.8	26.5	25.9	28.1	32.1
average	18.1	6.75	16.0	18.9	22.5	24.6	25.4	28.8	31.0	33.7	36.6	38.1	41.1	45.9
H1 <sub>acid-extracted</sub>	28.9	41.7	28.8	29.5	26.4	27.5	28.3	24.2	21.6	19.1	16.6	13.3	10.9	9.46
H2 <sub>acid-extracted</sub>	26.1	38.1	25.1	24.3	20.3	20.8	20.7	16.3	14.3	13.2	11.3	9.77	7.68	6.20
HR <sub>acid-extracted</sub>	43.5	44.2	44.6	45.3	44.5	45.0	45.4	41.9	40.7	38.0	35.3	31.2	27.5	25.9
average	32.8	41.3	32.8	33.0	30.4	31.1	31.5	27.5	25.5	23.4	21.0	18.1	15.4	13.9
H1 <sub>organic</sub>	3.78	7.44	5.54	6.57	7.90	9.31	8.90	8.59	7.47	6.15	5.61	4.79	4.35	3.80
H2 <sub>organic</sub>	3.68	8.09	5.60	6.38	7.74	8.19	8.08	7.20	6.43	6.11	5.26	4.71	3.98	3.67
HR <sub>organic</sub>	6.05	9.47	8.89	9.90	11.8	12.1	12.7	12.2	11.4	10.6	10.0	9.34	9.83	10.0
average	4.50	8.33	6.68	7.62	9.14	9.87	9.88	9.33	8.45	7.60	6.96	6.28	6.06	5.84
H1 <sub>residual</sub>	51.0	43.2	50.7	45.8	44.2	39.8	39.5	40.4	42.0	41.4	41.7	42.7	41.6	38.4
H2 <sub>residual</sub>	43.9	44.7	46.2	42.5	40.5	37.1	36.1	37.0	37.9	37.0	36.4	36.3	36.4	33.0
HR <sub>residual</sub>	39.1	43.0	36.8	33.0	29.1	26.6	24.2	25.9	25.1	27.6	28.2	33.6	34.6	31.9
average	44.6	43.6	44.6	40.4	38.0	34.5	33.3	34.4	35.0	35.3	35.4	37.5	37.5	34.4

bonate and Fe–Mn oxides fractions were separately extracted (Tessier *et al.*, 1979). However, in our procedure, these three fractions were combined into one step in order to reduce the contamination of REEs from reagent and preconcentration procedures.

The first stage of the process is extraction by diluted 0.2 N HCl. This step extracts the exchangeable fraction that is bound to carbonates and Fe–Mn oxides, and is known as the “acid-extracted fraction” (Tessier *et al.*, 1979). The second step is extraction by diluted HNO<sub>3</sub> acid mixed with H<sub>2</sub>O<sub>2</sub> (30% v/v) at pH ~2, to obtain the “organic (bound-to-organic-matter) fraction.” These two fractions (acid- and organic-) are together defined as the “labile fraction,” and the residual solid phase after these two extraction steps is defined as the “residual fraction” of the REE measurement. The extractants of the REE concentrations during the first (acid-extracted) and second (organic fractions) procedures were measured by ICP-MS after pre-treatment by acid. The residual fraction was decomposed by mixing acid of HF, HNO<sub>3</sub>, and HClO<sub>4</sub>, and then their REE concentrations were also measured by ICP-MS.

## RESULTS

The measured hydrographic properties, i.e., temperature, pH, DO, and concentrations of the major anions and cations in the lake and river waters are given in Supplementary Table S1. The concentrations of REEs in the dissolved, acid-extracted, organic, and residual fractions are listed in Supplementary Tables S2 to S5.

### *Hydrogeological characteristics*

The lake and river waters are primarily HCO<sub>3</sub><sup>-</sup>–Ca (Lake Hongfeng and its tributaries) or SO<sub>4</sub><sup>2-</sup>–HCO<sub>3</sub><sup>-</sup>–Ca (Lake Aha and its tributaries) water types. Their pH ranges from 7.7 to 8.8, with the average value of 8.4. This reflects the importance of limestone and dolomite dissolution of in the studied watershed. The major element compositions of Lake Hongfeng and its inflowing river waters are dominated by the HCO<sub>3</sub><sup>-</sup> and the Ca<sup>2+</sup>. HCO<sub>3</sub><sup>-</sup> accounts for about 70% of the total anions and Ca<sup>2+</sup> accounts for about 70% of the total cations. The relative contributions of major ions in Lake Aha and its inflowing tributary waters also showed the same predominant carbonate weathering. However, the absolute concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> in Lake Aha and its river waters are approximately double those of the Lake Hongfeng water.

Very high concentrations of dissolved Mn accompanying the very high concentrations of SO<sub>4</sub><sup>2-</sup> were observed in Lake Aha and its river water. This is probably caused by the existence of abundant coal stratum within the carbonate stratum near Lake Aha, and related coal-mining activities in the Lake Aha drainage basin.

### *Dissolved REEs*

The concentrations of dissolved REEs in the Hongfeng and Aha lake waters are considerably lower than those previously reported for rivers, and are similar to the REEs concentrations of seawater (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990). For example, the concentrations of dissolved Nd in the Lake Hongfeng and Lake Aha is mainly 5–20 pmol/kg, which is close to the value of coastal seawater (>10 pmol/kg) but higher than that of surface water in the open ocean (<5 pmol/kg) in the North Pacific (De Baar *et al.*, 1983; Murphy and Dymond, 1984; German and Elderfield, 1990; Piepgras and Jacobsen, 1992; Murray and Leinen, 1993; German *et al.*, 1995; Zhang and Nozaki, 1996; Alibo and Nozaki, 1999; Greaves *et al.*, 1999; Hongo *et al.*, 2006). However, these values are also much lower than the average value of previously reported Nd concentrations of world rivers (250 pmol/kg) and European and American rivers (1360 pmol/kg) (Elderfield *et al.*, 1990).

All the studied river waters, excepting HR3 River from the tributary of Lake Hongfeng, exhibit similar dissolved REE concentrations to that of the lake water samples. Sample HR3 River exhibits an Nd concentration of 135 pmol/kg. This high concentration can be attributed to the presence of a sewage drain from a chemical fertilizer factory close to the sample site. This implies that human activity can affect the REE concentration of surface waters.

### *REEs in different fractions of SPM*

The calculated proportions of the acid-extracted, organic, and residual fractions relative to the total REEs in the SPM can provide important information regarding the partition behavior of REEs in surface water. For Lake Aha, these proportions are acid-extracted (49%) > residual (39%) > organic (12%) while in Lake Hongfeng, the proportions are residual (60%) > acid-extracted (30%) > organic (10%) (Table 1). This demonstrates that the SPM REE compositions are different in the two lakes, with Lake Aha having a greater proportion of acid-extracted REEs than Lake Hongfeng.

## DISCUSSIONS

### *Controlling factors of dissolved REEs*

REE solubility is greatly influenced by pH, with REE concentrations increasing with decreasing pH (Elderfield *et al.*, 1990; Smedley, 1991). It is believed that the pH-controlled behavior of REEs is primarily due to adsorption of Fe–OH oxide loads (Elderfield *et al.*, 1990; Smedley, 1991). Figure 2 shows the relationship between pH and REE concentrations of our samples from the two alkaline lakes, Aha and Hongfeng, as well as global terrestrial surface waters. Three groups were identified (Fig.

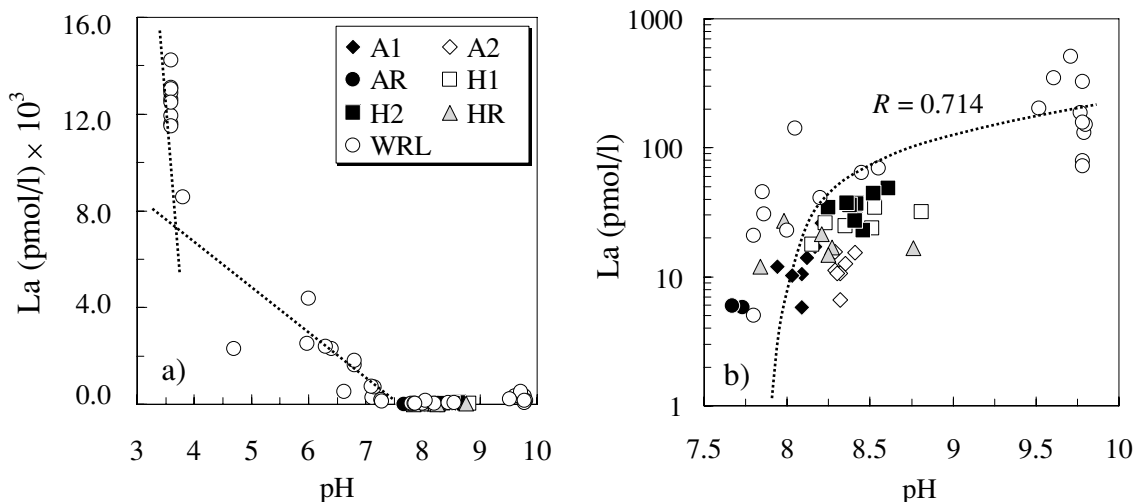


Fig. 2. Concentrations of dissolved La in the Aha and Hongfeng lake waters as a function of pH (a, pH 3–10; b, pH 7.5–10). WRL, world river and lake waters.

2a). When  $\text{pH} < 3.5$ , the dissolved REE concentrations in surface waters acutely decreases with increasing pH. In the pH range of 3.5–7.5, which covers most reported surface waters, the REE concentrations decrease linearly with increasing pH, but this is not so marked as for  $\text{pH} < 3.5$ . This is because when  $\text{pH} < 3.5$ , the geochemical behavior of REEs as well as Al, Si and most other trace elements is mainly controlled by chemical weathering of clay minerals (Dong *et al.*, 2000). For  $\text{pH} 3.5\text{--}7.5$ , REE behavior is mainly controlled by ion exchange and adsorption of Fe- and Mn-oxyhydroxide loads (Elderfield *et al.*, 1990; Smedley, 1991). For  $\text{pH} > 7.5$ , REE concentrations increase with pH increases (Fig. 2b). An accepted interpretation is that at  $\text{pH} \sim 7\text{--}7.5$ , Fe- and Mn-oxyhydroxide loads, which are the main carriers of dissolved REEs and especially light rare earth elements (LREEs) in surface waters, will be unstable and removed from the solution phase to SPM (Elderfield *et al.*, 1990; Smedley, 1991). This would cause a considerable decrease of the concentrations of dissolved REEs in surface waters. This is why the lowest REE concentration is always observed in the neutral and alkaline surface waters (Goldstein and Jacobsen, 1988). Moreover, when  $\text{pH} > 7.5$ , REE concentrations slightly increase with increasing pH (Fig. 2b). This phenomenon has not been reported in the previous studies. We assume that, in this stage, REE behavior is controlled by complicated factors such as  $\text{HCO}_3^-$  complexation.

This “three stage model” for the relationship between REE concentration and pH implies that the geochemical behavior of dissolved REEs in surface waters is mainly controlled by pH.

#### Partition of REEs in SPM fractions

The two lakes exhibit different REE compositions within their SPM. Lake Aha has a higher proportion of acid-extracted REEs than Lake Hongfeng. This is because the SPM in the Lake Aha has a greater concentration of Fe–Mn oxides. Very high concentrations of Mn were observed not only in the dissolved phase as mentioned above, but also observed in the acid-extracted fraction of Lake Aha and its river waters (Table S3).

Moreover, the results also indicated that the concentrations of acid-extracted REEs in the SPM from Lake Hongfeng were nearly two times higher than that of SPM from the Hongfeng rivers. This suggests that SPM in the Lake Hongfeng is derived not only from its inflow rivers but also produced within the lake. While proportions of the chemical extracted and residual fractions of SPM is nearly identical in the Lake Aha river water, although the river water SPM has higher REE concentration than the lake waters. This implies that SPM in the Lake Aha is derived from the same sources as that of the Aha River.

In general, the percentage of the “labile fraction” of SPM from the Aha and Hongfeng lakes and their river waters are much higher than that of large rivers such as the Yangtze River and the Huanghe River of China, maybe due to their weak hydrodynamic conditions. SPM collected from large rivers has a higher percentage of residual fractions (Wang and Liu, 2008).

#### REE fractionation among dissolved and extracted phases of SPM

In waters of the Hongfeng and Aha river-lake regimes, the REEs in the dissolved, acid-extracted, organic and

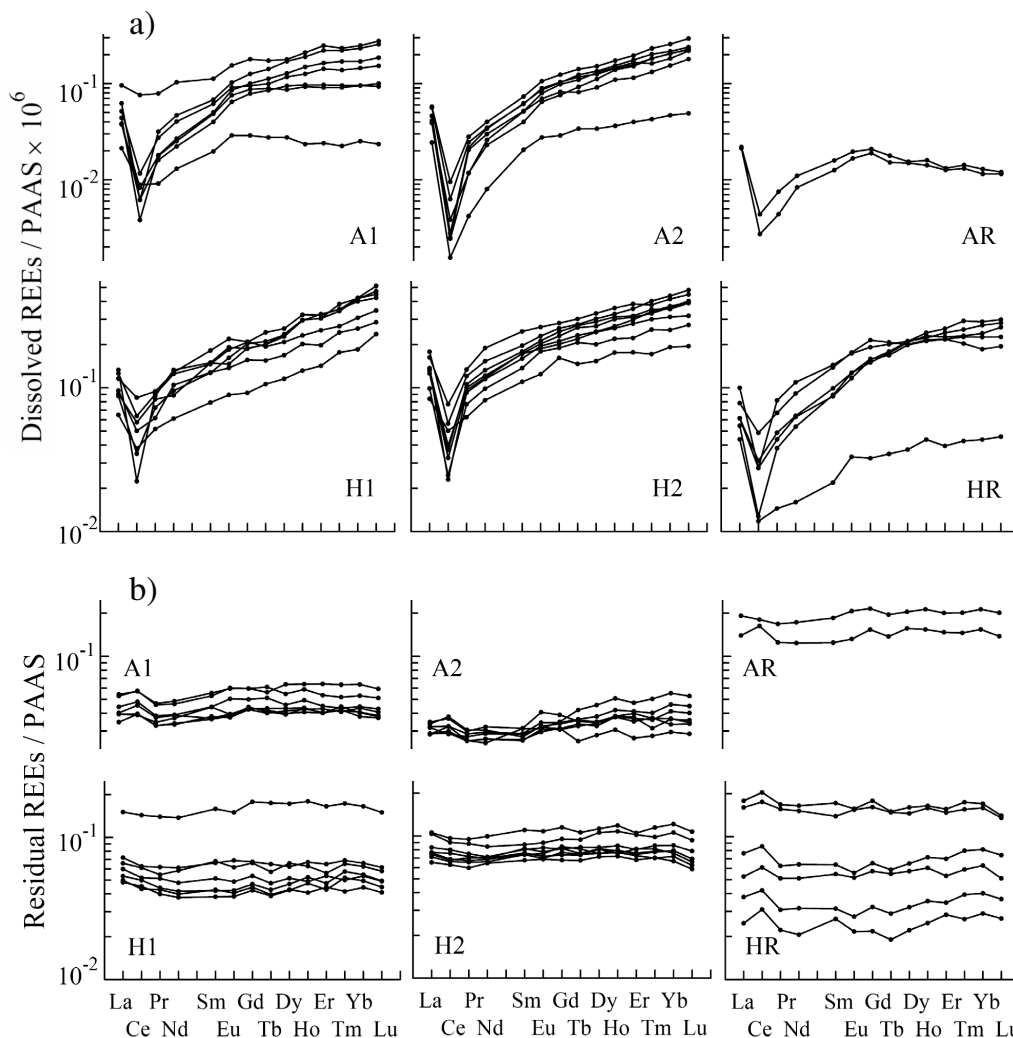


Fig. 3. Shale (PAAS) normalized patterns of a) dissolved REEs and b) residual REEs of suspended particulate matter in the Aha (A1, A2) and Hongfeng (H1, H2) lake waters and their tributary waters (AR, HR).

residual fractions show different shale (PAAS)-normalized patterns (Figs. 3a, 3b, 4a and 4b).

The residual material of the SPM exhibits flat PAAS-normalized REE patterns both for the Hongfeng and Aha lakes and their river waters (Fig. 3b).

The dissolved REEs in the Hongfeng and Aha lake waters show clearly heavy rare earth elements (HREEs) enrichment and LREE depletion, with the  $[Yb/La]_N$  values of 2–5 to as high as that of seawater (Fig. 3a). According to the published data, the highest observed  $[Yb/La]_N$  value of ~100–200 was found in Lake Mono, reported by Johannesson and Lyons (1994). Similar to Hongfeng and Aha Lakes, Lake Mono also is an alkaline lake with pH as high as 9.8. This implies that the LREEs are preferentially removed by Fe–Mn oxides compared to HREEs when they scavenge in alkaline waters, lead-

ing to HREE enrichment in filtrated waters. This is why the low REE concentration and accompanying HREE enrichment pattern was commonly observed in high pH, alkaline waters.

The acid-extracted and the organic REEs of the Aha Lake and river SPM show a standard convex PAAS-normalized pattern (Figs. 4a and 4b). Similar results have been reported for the acid-soluble fraction of river particles (Sholkovitz *et al.*, 1994), indicating that the labile fraction of SPM contains a higher proportion of both middle rare earth elements (MREEs) and LREEs than HREEs. However, in Lake Hongfeng and its river waters, only half of the acid-extracted fraction of water samples display convex shale-normalized pattern, while the other samples display a progressive HREE depletion pattern with slight MREE enrichment (Fig. 4b). This could be

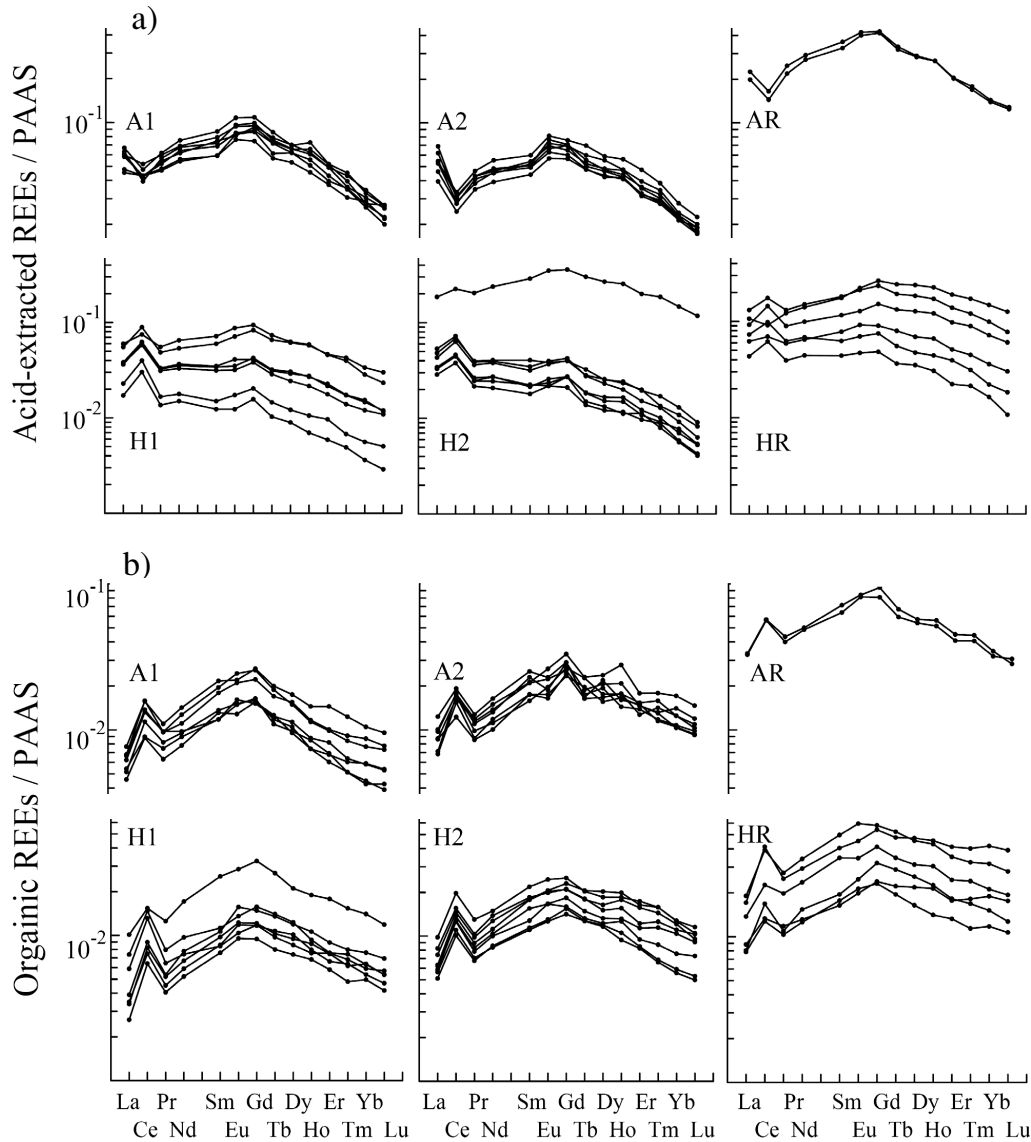


Fig. 4. Shale (PAAS) normalized patterns of a) acid-extracted REEs and b) organic REEs of suspended particulate matter from the Aha (A1, A2) and Hongfeng (H1, H2) lake waters and their tributary waters (AR, HR).

due to the fact that the Aha lake waters have more dissolved and particulate Mn than the Hongfeng lake waters. The high concentration of acid-extracted Mn in the SPM could preferentially adsorb MREEs.

#### La anomaly

Although much research regarding REE anomalies has been conducted, the formation mechanisms of some REE anomalies, such as La anomalies, are still unclear. Slight positive La anomalies are reported in some ocean waters relative to freshwater and shale (Bau and Dulski, 1996; Zhang and Nozaki, 1996; Shields and Webb, 2004; Lawrence and Kamber, 2006), but, similar to strong negative

Ce anomalies, it is difficult to conclude that a positive La anomaly is a unique feature of marine REE patterns.

There is no universally approved method for calculating La anomalies, which is sometimes defined as  $[La]_N^* = [Pr]_N + 2 \times ([Pr]_N - [Nd]_N)$  (Lawrence *et al.*, 2006). In the present research, the PAAS normalized La/Nd ratio ( $[La/Nd]_N$ ) has been used to discuss the La anomaly. This is because most reported  $[La/Nd]_N$  values for dissolved REEs in surface waters are nearly 1 (0.9–1.1) (Goldstein and Jacobsen, 1988), therefore, we can identify the negative or positive La anomaly when the  $[La/Nd]_N$  ratio lower than 0.9 or higher than 1.1.

The  $[La/Nd]_N$  of the dissolved REEs in water samples

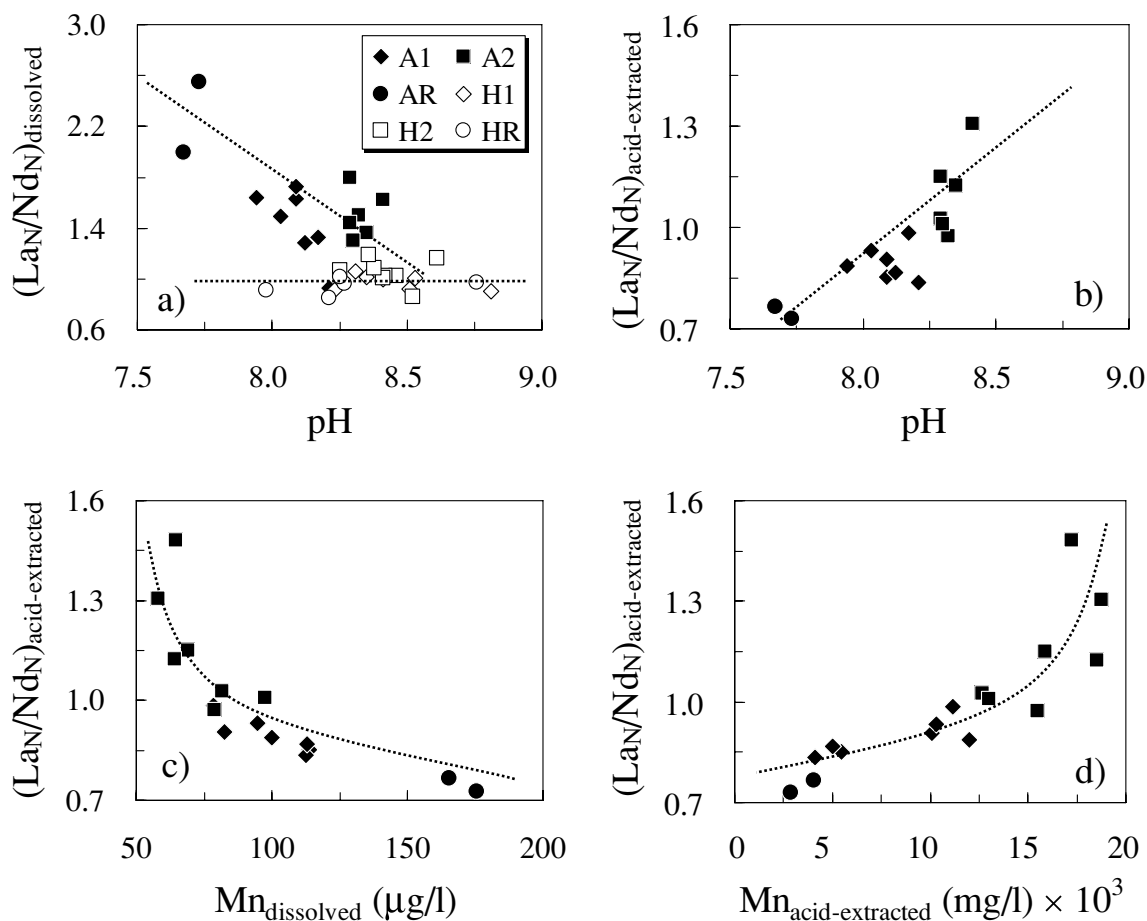


Fig. 5. Shale-normalized La/Nd ratios of a) dissolved REEs from the Aha and Hongfeng lakes and their river waters and b) acid-extracted REEs from Lake Aha and its river waters as a function of pH. Variation of shale-normalized La/Nd ratios of acid-extracted fractions from Lake Aha and its river waters with varying concentrations of c) dissolved Mn and d) acid-extracted Mn.

from Lake Hongfeng and its rivers show relatively constant values close to 1 (0.86–1.15), indicating the absence of an La anomaly (Fig. 5a). However, the  $[La/Nd]_N$  ratios of dissolved REEs of Lake Aha and its river water show variable values of 0.93–2.55 with an average value of 1.7 (Fig. 5a). This suggests that distinct positive La anomalies for dissolved REEs occurred in the Lake Aha and its river waters. Since Lake Aha and Lake Hongfeng are located within the same drainage basin, the different  $[La/Nd]_N$  ratios of dissolved REEs between the two lakes implies that the La anomaly is more likely caused by hydrogeochemical processes rather than rock weathering.

A possible explanation is that removal of LREEs leads to the expression of a positive La anomaly. It could also be caused by selective removal or preferential remobilization of La compared to the other LREEs between the dissolved and SPM phases (e.g., Sholkovitz *et al.*, 1994). The positive La anomaly in the acid-extracted fraction that was also observed can also be explained by the above assumption that preferential remobilization of

La from the solution onto the surface coatings of the suspended particles is more extensive (Fig. 5b). This explanation is further supported by the correlation between the  $[La/Nd]_N$  ratios of the acid-extracted REEs and the concentration of dissolved and acid-extractable Mn (Figs. 5c and 5d). This implies that the behavior of Mn, especially its transition between dissolved and particulate oxide fractions, is the major influence upon the formation of La anomalies.

Some reported positive La anomalies in surface waters have also been thought to be the result of anthropogenic pollution (Kulaksiz and Bau, 2011). The Aha lake and river waters have extremely high concentrations of dissolved Mn and  $SO_4^{2-}$  which are most likely due to pollution caused by nearby coal-mining activity. This may also be the cause of, or at least, contribute to the positive La anomaly seen in the dissolved phase.

#### Cerium anomaly

Ce anomalies are commonly observed in surface wa-



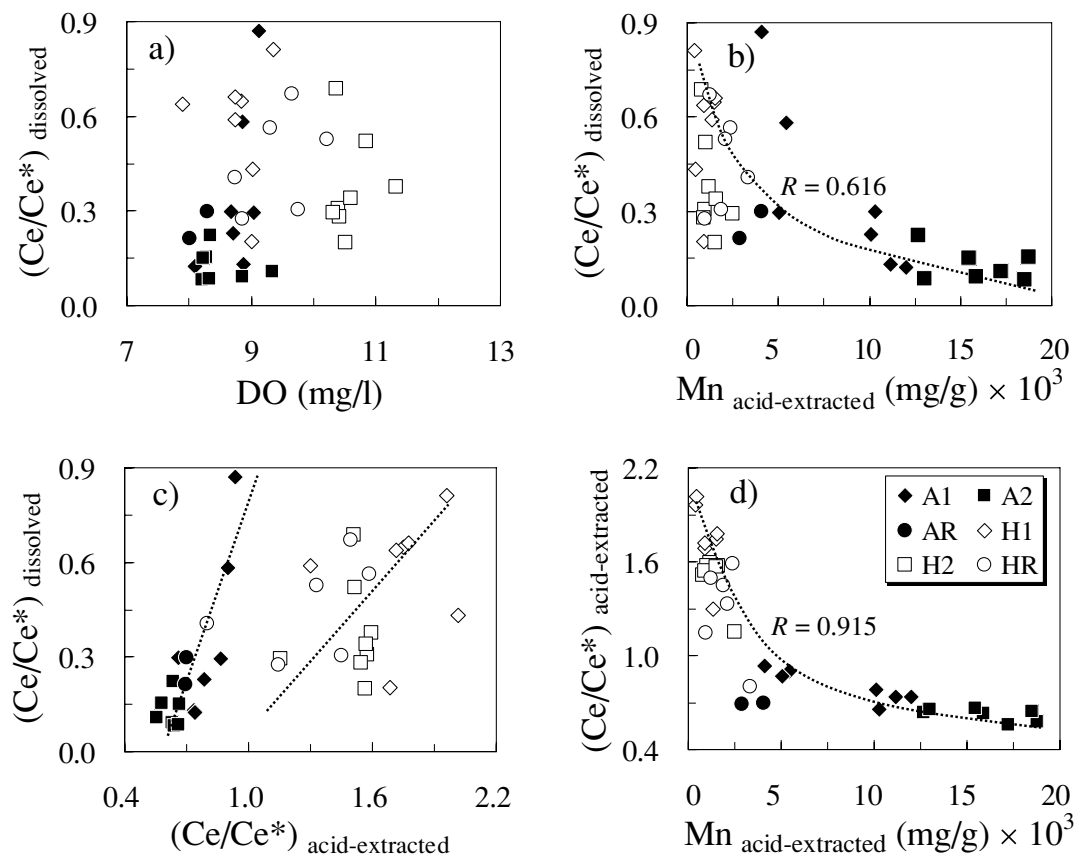


Fig. 6. Ce anomalies of a) dissolved REEs plotted against the concentrations of DO, b) acid-extracted REEs and c) the concentrations of acid-extracted Mn in the Aha and Hongfeng lakes and their river waters. d) Ce anomalies of acid-extracted REEs plotted against the concentrations of acid-extracted Mn.

ters due to the element's sensitive redox properties. Formation of negative Ce anomalies can be expected because Ce(III) is oxidized to insoluble Ce(IV) and the Ce(IV) tends to be more rapidly removed by particle scavenging than the other REE(III)s (Sholkovitz and Elderfield, 1988; Sholkovitz, 1993; Moffett, 1994). As a result, marked negative Ce anomalies are a REE feature of marine waters, but are also commonly reported in lakes and rivers, especially in alkaline and saline waters with high pH (Elderfield *et al.*, 1990; Sholkovitz, 1993).

As discussed in the previous section, positive La anomalies were observed in the dissolved phase of Aha lake waters, therefore, it is not suitable to calculate the Ce anomaly using the conventional method based on La and Pr or Nd. To avoid a result that is simply an artifact of the demonstrated positive La anomaly, the Ce anomaly was defined as  $Ce/Ce^* = 2 \times [Ce]_N / ([Pr]_N + [Nd]_N)$ . The calculated results show that all dissolved phases of the studied surface waters exhibit negative Ce anomalies with  $[Ce/Ce^*]_{PAAAS}$  values varying from 0.1 to 0.9 (Fig. 6a). Especially in the Aha Lake waters, most of the dissolved REEs display a pronounced negative Ce anomaly of  $<0.3$ .

Negative Ce anomalies of dissolved REEs in Lake Hongfeng and its river waters ranging from 0.2 to 0.9 are higher than that of Lake Aha, indicating the Fe- or Mn-oxide scavenging processes are more intensive in the Lake Aha and its river waters.

Ce anomalies were also observed in the acid-extracted and organic fractions of both lakes (Figs. 4 and 6b). In Lake Hongfeng Lake and its river waters, both the acid-extracted and organic REEs show positive Ce anomalies. However, in Lake Aha and its river waters, the acid-extracted REEs display a negative Ce anomaly while the organic REEs display a positive Ce anomaly. In the previous studies, the REEs of all phases the chemical extractions of SPM show positive Ce anomalies (Moffett, 1994; Sholkovitz *et al.*, 1994; De Carlo *et al.*, 1998). This is because suspended particles are enriched in Ce by oxidative sorption, which produces a positive Ce anomaly. In Lake Aha and its river waters, the large negative Ce anomaly of the acid-extracted REEs could imply that intensive water-particle interactions occur in this location. However, when the acid-extracted REEs of Lake Aha and its river waters were normalized by dissolved REEs rather

than shale (PAAS), the Ce anomalies also show positive values, indicating preferential enrichment of Ce in the suspended particles.

The Ce anomalies of dissolved REEs were only weakly correlated with the concentrations of DO, but there was a good correlation between Ce anomalies of and Mn within the acid-extracted phase (Figs. 6c and 6d). This indicates that water-particle interaction processes promoted by Mn behavior are very important in the studied alkaline. Mn is an important metal for controlling the dissolved concentration of REEs in surface waters, because redox reactions can occur with Mn as the agent, especially in surface waters that contain very high concentrations of Mn as seen in Lake Aha and its rivers. The positive correlations of Ce with the redox sensitive species Mn indicates that Ce anomalies in the studied lake and river waters are, at least in part, redox controlled (Figs. 6c and 6d). The differences in behavior of the Ce between Aha and Hongfeng Lakes and their river waters may be partly influenced by adsorption onto oxide surfaces, because dissolved or acid-extracted fractions of Lake Aha and its river waters are more enriched in Mn than Lake Hongfeng and its river waters. It is again proposed that the Ce anomaly in the river or lake waters develops due to oxidative scavenging at Mn-oxide surfaces (De Carlo *et al.*, 1998).

### CONCLUSIONS

Analysis of the REE geochemistry of waters and suspended particles from two typical alkaline lakes, located in the South China Karst region, was conducted in this study. The results are summarized as follows:

(1) The linear relationship between pH and REE concentrations of global terrestrial surface waters over a wide pH range shows a “three stage model,” implying that the geochemical behavior of dissolved REEs in surface waters is mainly controlled by pH. The concentrations of dissolved REEs in the studied alkaline lake and river waters are much lower than most other terrestrial surface waters in the world due to their high pH.

(2) REEs in the dissolved phase and labile and residual fractions of SPM show different shale-normalized patterns. Shale-normalized patterns of dissolved REEs mainly show marked HREE enrichment, while acid-extracted and organic REEs mainly show convex patterns and the residual fractions have flat patterns.

(3) Uncommonly distinct positive La anomalies for dissolved REEs were observed in Lake Aha and its river waters in this study. A possible explanation is that Mn behavior is the major factor in the formation of La anomalies.

(4) The shale-normalized REEs patterns of the dissolved phase show a very large negative Ce anomaly in all studied water samples. Positive Ce anomalies were

observed in the acid-extracted and organic fractions. The positive correlation of Ce anomalies with the redox sensitive species Mn indicates that redox reactions are the main process controlling the Ce anomalies in the studied lakes.

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### REFERENCES

- Alibo, D. S. and Nozaki, Y. (1999) Rare earth elements in seawater: Particle association, shale-normalization, and Ce oxidation. *Geochim. Cosmochim. Acta* **63**, 363–372.
- Bau, M. and Dulski, P. (1996) Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth Planet. Sci. Lett.* **143**, 245–255.
- Byrne, R. H. and Kim, K.-H. (1990) Rare earth element scavenging in seawater. *Geochim. Cosmochim. Acta* **54**, 2645–2656.
- Byrne, R. H. and Lee, J. H. (1993) Comparative yttrium and rare-earth element chemistries in seawater. *Mar. Chem.* **44**, 121–130.
- De Baar, H. J. W., Bacon, M. P. and Brewer, P. G. (1983) Rare-earth distributions with a positive Ce anomaly in the western North Atlantic Ocean. *Nature* **301**, 324–327.
- De Carlo, E. H., Wen, X.-Y. and Irving, M. (1998) The influence of redox reactions on the uptake of dissolved Ce by suspended Fe and Mn oxide particles. *Aquatic Geochem.* **3**, 357–389.
- Dong, H., Qiu, R. and Lu, Y. (2000) Releasing of Si<sup>2+</sup> and Al<sup>3+</sup> under simulated acid rain in south China. *Environ. Sci.* **21**, 75–77 (in Chinese with English abstract).
- Elderfield, H., Upstill-Goddard, R. and Sholkovitz, E. R. (1990) The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochim. Cosmochim. Acta* **54**, 971–991.
- German, C. R. and Elderfield, H. (1990) Rare earth elements in the NW Indian Ocean. *Geochim. Cosmochim. Acta* **54**, 1929–1940.
- German, C. R., Masuzawa, T., Greaves, M. J., Elderfield, H. and Edmond, J. M. (1995) Dissolved rare earth elements in the Southern Ocean: Cerium oxidation and the influence of hydrography. *Geochim. Cosmochim. Acta* **59**, 1551–1558.
- Goldstein, S. J. and Jacobsen, S. B. (1988) Rare earth elements in river waters. *Earth Planet. Sci. Lett.* **89**, 35–47.
- Gosselin, D. C., Smith, M. R., Lepel, E. A. and Laul, J. C. (1992) Rare earth elements in chloride-rich groundwater, Palo Duro Basin, Texas, USA. *Geochim. Cosmochim. Acta* **56**, 1495–1505.
- Greaves, M. J., Elderfield, H. and Sholkovitz, E. R. (1999) Aeolian sources of rare earth elements to the Western Pa-

- cific Ocean. *Mar. Chem.* **68**, 31–37.
- Hongo, Y., Obata, H., Alibo, D. S. and Nozaki, Y. (2006) Spatial variations of rare earth elements in North Pacific surface water. *J. Oceanogr.* **62**, 441–455.
- Johannesson, K. H. and Lyons, W. B. (1994) The rare earth element geochemistry of Mono Lake water and the importance of carbonate complexing. *Limnol. Oceanogr.* **39**, 1141–1154.
- Koepfenkastro, D. and De Carlo, E. H. (1993) Uptake of rare earth elements from solution by metal oxides. *Environ. Sci. Technol.* **27**, 1796–1802.
- Kulaksztz, S. and Bau, M. (2011) Rare earth elements in the Rhine River, Germany: First case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere. *Environ. Int.* **37**, 973–979.
- Lawrence, M. G. and Kamber, B. S. (2006) The behaviour of the rare earth elements during estuarine mixing-revisited. *Mar. Chem.* **100**, 147–161.
- Lawrence, M. G., Greig, A., Collerson, K. D. and Kamber, B. S. (2006) Rare Earth Element and Yttrium Variability in South East Queensland Waterways. *Aquatic Geochem.* **12**, 39–72.
- Moffett, J. W. (1994) A radiotracer study of cerium and manganese uptake onto suspended particles in Chesapeake Bay. *Geochim. Cosmochim. Acta* **58**, 695–703.
- Murphy, K. and Dymond, J. (1984) Rare earth element fluxes and geochemical budget in the eastern equatorial Pacific. *Nature* **307**, 444–447.
- Murray, R. W. and Leinen, M. (1993) Chemical transport to the seafloor of the equatorial Pacific Ocean across a latitudinal transect at 135°W: tracking sedimentary major trace, and rare earth element fluxes at the equator and the intertropical convergence zone. *Geochim. Cosmochim. Acta* **57**, 4141–4163.
- Négrel, P., Grosbois, C. and Kloppmann, W. (2000) The labile fraction of suspended matter in the Loire River (France): multi-element chemistry and isotopic (Rb–Sr and C–O) systematics. *Chem. Geol.* **166**, 271–285.
- Piegras, D. J. and Jacobsen, S. B. (1992) The behavior of rare earth elements in seawater: Precise determination of variations in the North Pacific water column. *Geochim. Cosmochim. Acta* **56**, 1851–1862.
- Shabani, M. B., Akagi, T., Shimizu, H. and Masuda, A. (1990) Determination of trace lanthanides and yttrium in seawater by inductively coupled plasma mass spectrometry after preconcentration with solvent extraction and back extraction. *Anal. Chem.* **62**, 2709–2714.
- Shields, G. A. and Webb, G. E. (2004) Has the REE composition of seawater changed over geological time. *Chem. Geol.* **204**, 103–107.
- Sholkovitz, E. R. (1993) The geochemistry of rare earth elements in the Amazon River estuary. *Geochim. Cosmochim. Acta* **57**, 2181–2190.
- Sholkovitz, E. R. and Elderfield, H. (1988) Cycling of dissolved rare earth elements in Chesapeake Bay. *Global Biogeochem. Cycles* **2**, 157–176.
- Sholkovitz, E. R., Landing, W. M. and Lewis, B. L. (1994) Ocean particle chemistry: the fractionation of rare earth elements between suspended particles and seawater. *Geochim. Cosmochim. Acta* **58**, 1567–1579.
- Smedley, P. L. (1991) The geochemistry of rare earth elements in groundwater from the Carnmenellis area, southwest England. *Geochim. Cosmochim. Acta* **55**, 2767–2779.
- Tanizaki, Y., Shimokawa, T. and Nakamura, M. (1992) Physicochemical speciation of trace elements in river waters by size fractionation. *Environ. Sci. Technol.* **26**, 1433–1444.
- Tessier, A., Campbell, P. G. C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844–851.
- Wang, Z.-L. and Liu, C.-Q. (2008) Geochemistry of rare earth elements in the dissolved, acid-soluble and residual phases in surface waters of the Changjiang Estuary. *J. Oceanogr.* **64**, 407–416.
- Wood, S. A. (1990) The aqueous geochemistry of the rare-earth elements and yttrium I. review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chem. Geol.* **82**, 159–186.
- Yan, X.-P., Kerrich, R. and Jim Hendry, M. (1999) Sequential leachates of multiple grain size fractions from a clay-rich till, Saskatchewan, Canada: implications for controls on the rare earth element geochemistry of porewaters in an aquitard. *Chem. Geol.* **158**, 53–79.
- Zhang, J. and Liu, C.-Q. (2004) Major and rare earth elements in rainwaters from Japan and East China Sea Natural and anthropogenic sources. *Chem. Geol.* **209**, 315–326.
- Zhang, J. and Nozaki, Y. (1996) rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the Western South Pacific Ocean. *Geochim. Cosmochim. Acta* **60**, 4631–4644.
- Zhang, J., Amakawa, H. and Nozaki, Y. (1994): The comparative behaviors of yttrium and lanthanides in the seawater of the North Pacific. *Geophys. Res. Lett.*, **21/24**: 2677–2680.

#### SUPPLEMENTARY MATERIALS

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Tables S1 to S5