

The behavior of rare earth elements in naturally and anthropogenically acidified waters

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Received 18 May 2005; received in revised form 12 July 2005; accepted 14 July 2005

Available online 13 December 2005

Abstract

In this paper, the behavior of rare earth elements (REE) in a watershed impacted by acid-mine drainage (Fisher Creek, Montana) is compared to that in a volcanically acidified watershed (Rio Agrio and Lake Caviahue, Argentina). The REE behave conservatively in acidic waters with pH values less than approximately 5.5. However, above pH 5.5, REE concentrations are controlled by adsorption onto or co-precipitation with a variety of Fe or Al oxyhydroxides. The heavy REE partition to a greater extent into the solid phase than the light REE as pH rises above 6. Concentrations of REE exhibit diel (24-h) cycling in waters that were initially acidic, but have become neutralized downstream. In Fisher Creek, at the most downstream sampling station investigated (pH 6.8), concentrations of dissolved REE were 190–840% higher in the early morning versus the late afternoon. This cycling can be related to temperature-dependent, cyclic adsorption–desorption of REE onto hydrous ferric or aluminum oxide or both. Similar but gentler diel cycling of the REE was found at Rio Agrio. The existence of such cycling has important ramifications for the study of REE in natural waters.

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Keywords: Rare earth elements; Acid-mine drainage; Diel; Diurnal; Acid waters

1. Introduction

Because of their coherent geochemical properties, the rare earth elements (REE) have received considerable attention as tracers of water–rock interaction in geologic environments. In the past decade, the REE have been investigated for their potential as tracers in acidic natural waters, both in systems in which the acidity is produced by natural processes [1–6] and in systems affected by human activities, e.g., mining-impacted environments [7–14]. In spite of the recent activity in this area, our understanding of the behavior of REE in acidic systems is still far from complete. Recently, we have reported results of measurements of the REE from a watershed impacted by mining activities (Fisher Creek, Montana) [15] and a watershed that is naturally acidic as a result of volcanic inputs (Rio Agrio–Lake Caviahue, Argentina) [16]. In this paper, we compare REE systematics of waters from Fisher Creek with those from the Argentinian watershed, based on the

results of our previous studies [15,16] and some new data from Argentina.

2. Brief description of study areas

Fisher Creek is a small, high-altitude, mountain stream located in the New World mining district, Montana, just north-east of Yellowstone National Park (Fig. 1). The headwaters of Fisher Creek are acidic due to drainage from abandoned mines that produced Cu–Au–Ag–Pb–Zn ore [17]. Downstream from the mine area, the pH of Fisher Creek increases due to the influx of relatively unpolluted tributaries and ground-water baseflow. Ocherous secondary precipitates are present over the entire length of Fisher Creek. The precipitates change from predominantly hydrous ferric oxide (HFO) in the headwaters, to a mixture of HFO and hydrous aluminum precipitates further downstream [15]. Three locations (F1, F2 and F3; see Fig. 1) along Fisher Creek were sampled simultaneously over a 24-h period on August 13–14, 2002. The 24-h average pH changed from 3.3 (F1), to 5.5 (F2), to 6.8 (F3) along the stream. The variation in pH at each station

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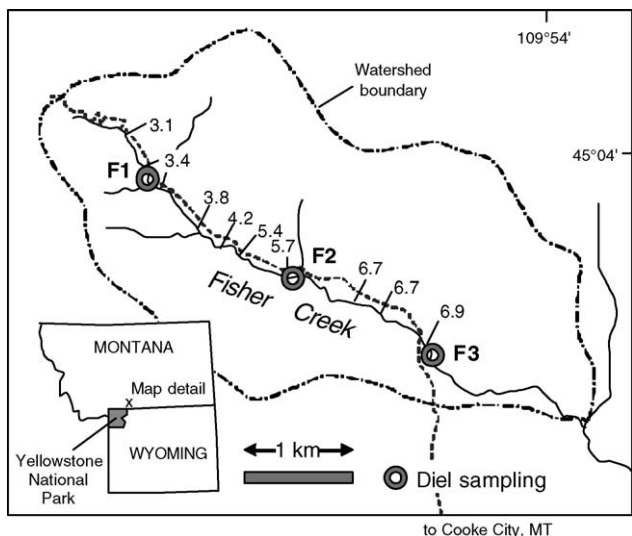


Fig. 1. Diel monitoring stations (shaded circles) and pH values measured on August 12, 2002, Fisher Creek, New World mining district, Montana.

over the 24-h period was remarkably small (± 0.1 units or less).

The Rio Agrio watershed is a drainage basin in northwest Patagonia, Argentina, near the border with Chile (Fig. 2). This watershed owes its acidity to volcanic inputs of HCl, HF and H₂SO₄ at the headwaters of the R. Agrio, which occur as a series of hot springs on the east flank of Copahue Volcano [18–21]. Copahue is an active stratovolcano (el. 2965 m) of predominantly andesitic composition, whose most recent eruption was during July–August of 2000 [18]. Although the R. Agrio is diluted by several tributary streams, it remains acidic for approximately 40 km downgradient from its source. Besides the R. Agrio itself, the watershed includes a hyperacidic (pH <1) volcanic crater lake, and a much larger glacially carved lake occupying a portion of the floor of an old caldera [22] (Fig. 2). Most of the samples from this watershed were obtained in March 2003, but a series of samples was taken at three different sites along the lower R. Agrio in March 2004 to examine diel variations in the REE content. The results of the 2003 campaign have

been reported in detail in ref. [16], but a summary of REE data for the 2004 campaign are reported here for the first time. A more detailed discussion of the 2004 data is given in ref. [23].

The upper R. Agrio slowly increases in pH from 1.5 at its source to 2.4 as it enters Lake Cavihue, the pH of which is approximately 2.7 (Fig. 2). In March 2003, the pH of the lower R. Agrio gradually rose to 4.7 just upstream of the confluence with R. Norquín. Below the confluence, abundant precipitates of hydrous Al oxide (HAO) formed, as the pH of the R. Agrio increased from 4.7 to 6.1. These precipitates imparted a turbid, milky appearance to the river at the confluence with R. Norquín. In March 2004, the pH rose to 6.3 and the water already was cloudy white at a site upstream of R. Norquín (Fig. 2).

3. Methods

Both filtered (0.45 μm) and non-filtered samples were taken of each water. The samples were preserved with 2% Fisher Optima high-purity HNO₃. The REE contents of water samples from all the locations investigated were determined by inductively coupled plasma-mass spectrometry (ICP-MS) at Washington State University. The analytical protocol varied somewhat, in part dependent on the expected REE concentrations. Some samples were analyzed for REE directly, and others required dilution. Typically, temperature, pH, conductivity and, less commonly, Eh were measured in the field. Alkalinity/acidity was determined by titration either in the field or as soon after sampling as practical. Samples also were typically analyzed for a variety of major and trace elements (inductively coupled plasma-atomic emission spectrometry) and anions (ion chromatography). For details of sampling and analytical procedures, the reader is referred to [15,16].

4. Results and discussion

4.1. Fisher Creek

The REE were found to behave conservatively, i.e., their concentrations were only affected by dilution, at the two more acidic, upstream stations (F1 and F2). This was evidenced by the facts that the dissolved REE load (concentration times discharge) was constant between F1 and F2, and the REE concentrations in filtered and non-filtered samples were essentially identical within analytical imprecision ($\pm 5\%$) (for more details, see [15]). On

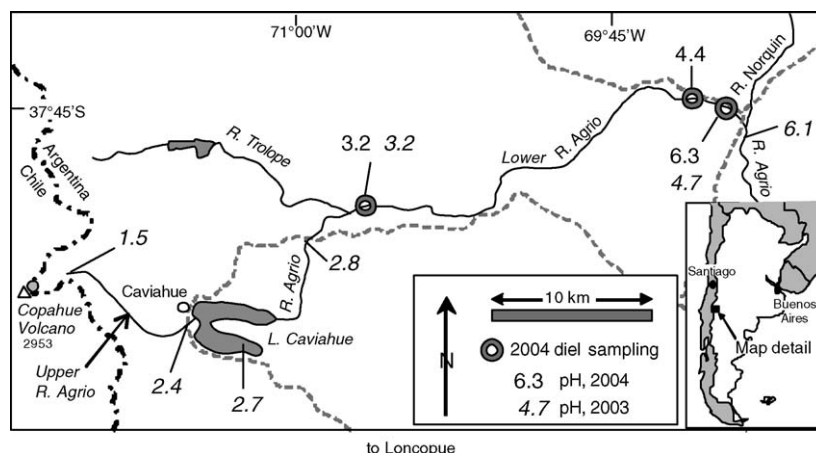


Fig. 2. Location map of the Rio Agrio watershed. Diel sampling sites are shown by the shaded circles. Selected values for stream pH are shown as measured in 2003 (italics) and 2004 (no italics).

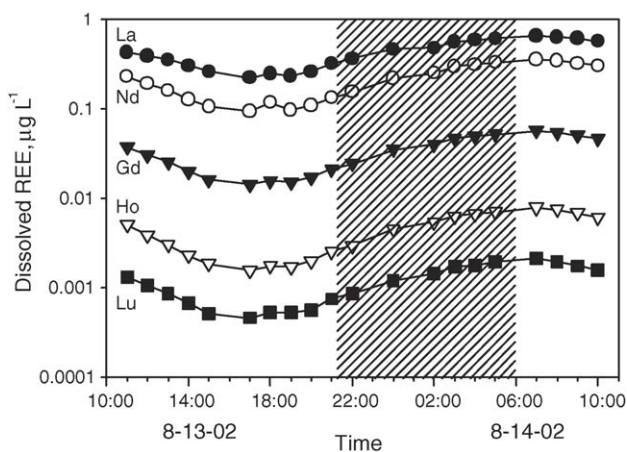


Fig. 3. Diel variations of the concentrations of dissolved La, Nd, Gd, Ho and Lu in Fisher Creek (site F3, pH 6.8). The shaded area denotes hours of darkness.

the other hand, at the downstream station (F3), REE partitioned into suspended particles to a degree that varied according to the time of day. Concentrations of dissolved REE were 190–840% higher in the early morning versus the late afternoon (Fig. 3). The decrease in dissolved REE concentration during the day coincided with a corresponding increase in REE as suspended particles (Fig. 4), such that diel changes in the total REE concentration were comparatively minor (27–54%). The dissolved REE concentrations correlate inversely with the temperature (Fig. 4).

In order to be better able to observe subtle variations in the behavior of the REE as a function of atomic number, it is customary to normalize measured REE concentrations to those in some standard, naturally occurring material, in order to remove the see-saw, even-odd abundance pattern (Oddo Harkins effect) that is a vestige of nucleosynthetic processes. In our case, we employed the North American Shale Composite (NASC [24]), which is also a close approximation of the composition of continental crust. Filtered samples at the downstream station showed a decrease in NASC-normalized REE concentrations across the lanthanide series, with positive La and Gd anomalies and a negative Eu anomaly [15]. As the creek warmed in the afternoon, the slope of the REE profile steepened and the magnitude of

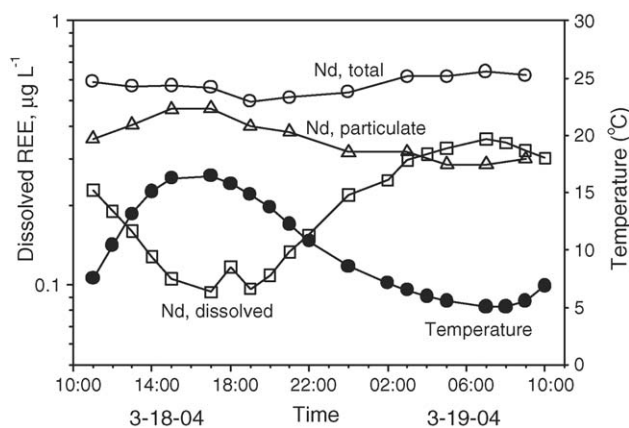


Fig. 4. Diel variations of total, dissolved, and particulate Nd concentrations and temperature, in Fisher Creek (site F3, pH 6.8).

the anomalies increased. These findings indicate that the heavier REE partitioned into the suspended solid phase to a greater extent than the light REE, consistent with previous field [13] and laboratory [25,26] investigations under similar conditions.

The above observations are explained by cyclic adsorption of REE onto suspended particles of hydrous ferric oxide (HFO). Partitioning of each rare earth element onto HFO relative to the aqueous phase reached a maximum at 17:00 h and a minimum at 05:00 h. This behavior is ascribed to diel changes in the temperature of the stream which drive changes in the thermodynamics of adsorption of the REE, possibly reinforced by kinetic factors (i.e., slower rates of reaction at night versus during the day). Estimates of the enthalpy of adsorption of each REE onto suspended HFO particles were calculated from the observed temperature dependence of the concentrations of REE in the aqueous phase, and averaged $+82.5 \pm 14$ kJ/mol [15]. These enthalpies are similar in magnitude to estimates in the literature for adsorption of divalent metal cations onto clays and hydrous metal oxides [27]. Diel variations in pH alone probably cannot account for the variation in REE because the total variation in pH at F3 was much smaller than that of temperature. However, the pH variations also showed a subtle diel variation in a direction that may have reinforced further the temperature effect.

4.2. Rio Agrio watershed

Based on the March 2003 samples, over the 40-km length of the R. Agrio sampled, the absolute concentrations of the dissolved REE decreased by several orders of magnitude owing to dilution and losses from adsorption or precipitation or both. However, dissolved REE concentrations normalized to fluoride concentration (fluoride was assumed to be conservative and have volcanic input as its only significant source) increased somewhat as pH increased from 1.6 at the source to 4.7 at a site on the lower R. Agrio just before its confluence with R. Norquín [16]. This is taken to indicate that the REE behaved conservatively at pH less than 4.7, and that until this point, REE concentrations were primarily affected by dilution. Little chemical attenuation occurred even though Fe oxyhydroxides were noted along the river bed along much of the lower R. Agrio. This is consistent with our findings at Fisher Creek [15] and those of Verplanck et al. [13], which indicate that the REE behave conservatively in streams impacted by mine drainage up to pH 5.5. Further downstream along the R. Agrio, where the pH increased to values above 6.0 and Al oxyhydroxides were noted to form, the fluoride-normalized REE concentrations dropped steeply, presumably owing to adsorption on the Al- and Fe-oxyhydroxides.

The NASC-normalized REE patterns of the water changed gradually throughout the watershed. The patterns were weakly heavy REE-enriched near the source of the Rio Agrio, exhibited a weak middle REE enrichment trend in Lake Caviahue, and then became weakly LREE-enriched in the lower reaches of the river [16]. The transition to a generally negative slope across the lanthanide series in the lower river is most likely a result of selective partitioning of the heavier REE into hydrous oxides of Fe and Al suspended in the water column, and accumulating on the river bed. Within Lake Caviahue, the REE concentrations did

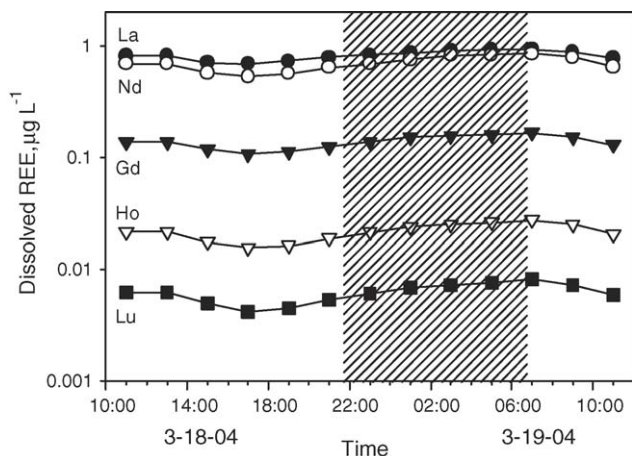


Fig. 5. Diel variations of the concentrations of dissolved La, Nd, Gd, Ho and Lu in the lower Rio Agrio (pH 6.3). The shaded area denotes hours of darkness.

not change significantly with depth. The behavior of the REE in Lake Caviahue and also in the crater lake at the summit of Copahue is discussed in more detail in ref. [16].

As at Fisher Creek, and consistent with conservative behavior, diel variations in the dissolved REE concentrations of Rio Agrio waters were not observed at the two more acidic sampling sites (pH 3.1 and 5.3) in March 2004. However, a weak cycle was observed in 2004 at the site, which had a pH of 6.3 (Fig. 5), although the magnitude of the diel variations was considerably smaller in the Rio Agrio compared to Fisher Creek. Moreover, the percentage of total REE present as filterable particles was much lower at the downgradient sampling site on the R. Agrio compared to the F3 site of Fisher Creek, probably owing to the steeper gradient and swifter current of the latter which would have allowed freshly formed particles to remain in suspension. In the lower Rio Agrio, both total and dissolved REE concentrations varied inversely with temperature (Fig. 6). Taken together, the data indicate that temperature-dependent adsorption is probably also the cause of diel variation in REE concentrations in the R. Agrio, but that the REE are adsorbing to solids along the river bed, rather than solids suspended in the water, as was the case at Fisher Creek. The gentler diel variations in the R. Agrio

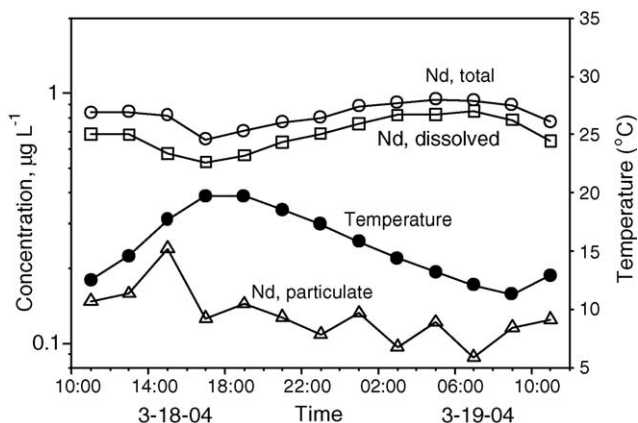


Fig. 6. Diel variations of total, dissolved, and particulate Nd concentrations and temperature, in the lower Rio Agrio (pH 6.3).

might be attributable to the slightly more acidic pH (6.3) at the R. Agrio site compared to the Fisher Creek site (6.8). Although the difference is only 0.5 pH units, this could result in large changes in the degree of adsorption if these pH values are near the adsorption edge for the REE onto Fe- and Al-oxyhydroxides, as seems likely. For example, data from our laboratory [28] show that adsorption of Nd and Gd onto goethite varies from ~50% at pH 6.3 to ~80% at pH 6.8. On the other hand, the gentler cycle may also be due to the gentler gradient of the R. Agrio compared to Fisher Creek, resulting in more of the suspended particles being removed to the river bed and thus less available for cycling.

5. Conclusions

One of the most important findings of our work is the discovery that REE concentrations in rivers with slightly acidic to near-neutral pH (~6.3–6.8) exhibit significant diel variations that can be attributed to temperature-dependent sorption reactions. Although diel cycling of other metals has been reported previously, we are unaware of any such reports for the REE prior to our studies. These results have obvious, important implications for the use of REE as tracers in many natural and mining-impacted waters. Subtle variations in REE data from different sample sites taken at different times of the day need to be interpreted with caution. We predict that diel variations in dissolved REE concentrations will be strongest in streams with slightly acidic to neutral pH (6–7), where hydrous Fe and Al oxides are forming and the system is at or near the pH adsorption edge for the REE, and where a relatively steep gradient keeps particles of hydrous Fe and Al oxides in suspension.

Our results also confirm the previously reported observation that the REE tend to behave conservatively in waters with pH less than approximately 5.5. Diel variations do not appear to occur in these lower pH waters because the REE are mostly in solution and there is therefore no significant temperature-dependent partitioning between the solution and solid phases.

Acknowledgements

We thank all the colleagues who contributed in one way or another to the work summarized in this paper, including Gustavo Baffico, Guadalupe Beamud, José M. De Giusto, Charles M. Knaack, Bethany J. Nelson, David A. Nimick, Fernando Pedrozo, Christopher L. Shope and Johan C. Varekamp. The research was supported by EPA-EPSCoR, International Exchange grant to Montana Tech from the U.S. Department of State, the Montana Board of Research and Commercialization, the U.S. Geological Survey Toxic Substances Hydrology Program and the USDA Forest Service.

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