

Hydrogeochemistry and rare earth element behavior in a volcanically acidified watershed in Patagonia, Argentina

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Abstract

The Rio Agrio watershed in northern Patagonia, Argentina is naturally acidic due to discharges of volcanic H₂SO₄, HCl, and HF at its headwaters near the summit of Copahue Volcano. A suite of water samples was collected from the summit of the volcano to a point roughly 40 km downstream where the pH of the Rio Agrio rose above 6.0. This suite included a sample of the hyperacidic (pH<1) crater lake at the summit of Copahue, the hot-spring source of the Upper Rio Agrio (pH<2), two depth profiles through Lake Caviahue (a large glacially-carved lake with pH~2.6, located 10 km east of the volcano summit), and several samples of the Lower Rio Agrio downstream of Lake Caviahue where pH increased due to the influx of tributary streams. Both filtered and non-filtered samples were collected and analyzed for major ions, trace metals, and rare earth elements (REE).

The concentrations of REE in the Rio Agrio decreased by several orders of magnitude through the study area, as a result of dilution and chemical attenuation. A subtle shift in the slope of shale-normalized profiles of dissolved REE concentration was observed, from being weakly positive near the source of the Rio Agrio, to showing a weak middle REE enrichment trend in Lake Caviahue, to being weakly negative in the lower reaches of the river. The trend to a negative slope across the lanthanide series in the lower river is explained by selective partitioning of the heavier REE to hydrous oxides of Fe and Al suspended in the water column, and accumulating on the riverbed. Most of the decrease in REE load occurred immediately downstream of the confluence with a tributary that increased the pH of the Rio Agrio from 4.3 to 6.1. Although the mixed water was supersaturated with REE phosphate compounds, precipitation of LnPO₄ is not believed to have been a dominant process because the predicted pattern of inter-element fractionation from phosphate deposition is inconsistent with the observed trends. Instead, REE attenuation most

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likely occurred from adsorption onto freshly precipitated hydrous aluminum oxide. The behavior of REE in the Rio Agrio watershed is broadly similar to what has been observed in watersheds that owe their acidity to oxidation of sulfide minerals. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The geochemistry of rare earth elements (REE) in acidic surface waters has been the focus of many recent investigations (Johannesson and Lyons, 1995; Johannesson et al., 1996; Lewis et al., 1997; Elbaz-Poulichet and Dupuy, 1999; Johannesson and Zhou, 1999; Gimeno et al., 2000; Leybourne et al., 2000; Åström, 2001; Worrall and Pearson, 2001a,b; Gammons et al., 2003, 2005; Verplanck et al., 2004; Bozau et al., 2004; Wood et al., 2005). Because different rock types typically have distinctive REE profiles, the REE are often used by geochemists as fingerprints of source regions. However, in low temperature aqueous environments, subtle differences in electronic configuration across the lanthanide series lead to differences in the behavior of REE with respect to aqueous complexation, ion adsorption, and mineral precipitation. Because of these differences, the REE may be fractionated during weathering and solute transport, leading to changes in the REE profiles in both solid and aqueous media. Although these fractionation processes are more pronounced in near-neutral or alkaline waters where the REE solubilities are low, REE fractionation has also been reported in acidic waters. For example, a number of studies have reported enrichments of the middle REE (relative to North American Shale Composite, or NASC) in lakes, rivers, and groundwaters with low pH (Johannesson et al., 1996; Elbaz-Poulichet and Dupuy, 1999; Johannesson and Zhou, 1999; Gimeno et al., 2000; Leybourne et al., 2000; Worrall and Pearson, 2001a,b). However, recent investigations have shown that contrary trends exist in acidic waters, including light REE enrichment (Bozau et al., 2004; Gammons et al., *in press*), heavy REE enrichment (Gammons et al., 2003), and middle REE depletion (Verplanck et al., 2004). Thus, it cannot be said that there is a general REE pattern that is universally characteristic of low pH waters.

Most previous studies of REE in acidic waters have focused on mining-impacted streams and lakes (e.g., Elbaz-Poulichet and Dupuy, 1999; Gimeno et al., 2000;

Leybourne et al., 2000; Åström, 2001; Worrall and Pearson, 2001a,b; Gammons et al., 2003, 2005; Verplanck et al., 2004; Bozau et al., 2004; Wood et al., 2005), or acid hot springs (Kikawada et al., 1993; Lewis et al., 1997; Wood, 2003). In contrast, there have been relatively few studies of REE in naturally-acidic lakes (Johannesson and Lyons, 1995; Johannesson and Zhou, 1999; Takano et al., 2004), and we are not aware of a previous investigation of REE in a naturally-acidic river. The focus of the present study is the Rio Agrio watershed, a drainage basin in northwest Patagonia, Argentina. This watershed owes its acidity to volcanic inputs of HCl, HF, and H₂SO₄ at the headwaters of the river, which occur as a series of hot springs on the east flank of Copahue Volcano (Goss, 2001; Varekamp et al., 2001, 2004, *in press*; Wendt-Potthoff and Koschorreck, 2002). Copahue is an active stratovolcano (el. 2965 m) of predominantly andesitic composition, whose most recent eruption was during July–August of 2000 (Varekamp et al., 2001). Although the Rio Agrio is diluted by several tributary streams, it remains acidic for more than 40 km downgradient from its hot-spring source (Fig. 1). Besides the Rio 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 (Pedrozo et al., 2001). Because of these unique features, the Copahue/Rio Agrio system affords an opportunity to examine the behavior of rare earth elements in a variety of lotic and limnic settings, all within a watershed that is naturally acidic. The results of this study provide an interesting contrast to investigations of REE in mining-impacted watersheds, and should be of interest to anyone dealing with the geochemistry of REE in acidic waters.

2. Methods

2.1. Field methods

Most of the water samples reported in this study were collected during March 20 to 24, 2003. Addi-

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