Rare earth elements as reactive tracers of biogeochemical weathering in forested rhyolitic terrain

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ABSTRACT

Rare earth elements (REEs) were evaluated as potential tracers of biogeochemical weathering at pedon, hillslope, and catchment scales in the Jemez River Basin Critical Zone Observatory (JRB-CZO), Valles Caldera National Preserve, NM, USA. We investigated time series of REE patterns in precipitation, soil pore water, groundwater, and stream water, and related these data to REE composition of soil, rock and atmospheric dust. REE signatures in stream waters are dynamic, reflecting processes that occur along hydrologic flowpaths during transport to the stream, including organic matter complexation, primary and secondary mineral weathering, water/soil/bedrock interaction, and atmospheric deposition. Strong compositional similarities for the REE between soil waters and stream waters during the initial snowmelt are consistent with shallow subsurface flows to streams. Most (bio) chemical denudation of REE occurred during the snowmelt-derived dissolved organic carbon (DOC) pulse, during which time apparent colloidal mobilization of REE occurred in association with Fe and Al (oxy)hydroxides. The REE and DOC concentrations in stream waters were positively correlated ($R^2 = 0.80$, $p < 0.0001$) during snowmelt, suggesting REE complexation and mobilization in association with organic ligands during the period of shallow subsurface flow. Positive Eu-anomalies occur in the soil matrix ($[Eu / Eu^*]_{RT}$ range from 1.79 to 2.52), soil solutions ($[Eu / Eu^*]_{RT}$ range from 1.89 to 5.98), and stream waters ($[Eu / Eu^*]_{RT}$ range from 1.01 to 2.27) with respect to the host lithologies—effects attributable to both eolian deposition and preferential feldspar dissolution. Cerium anomalies in soil solids and porewaters indicate seasonally dynamic translocation and oxidative accumulation in subsurface soil horizons (surface horizons: $[Ce / Ce^*]_{RT}$ range from 0.70 to 1.1; subsurface horizons: $[Ce / Ce^*]_{RT}$ range from 0.95 to 1.29), consistent with prior research reporting Ce(IV) co-precipitation with Fe- and Mn-oxide minerals.

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1. Introduction

Prior studies have shown the potential for lanthanide series metals (i.e., "rare earth elements" or REE) to serve as reactive tracers of biogeochemical processes in low temperature systems (e.g., Elderfield et al., 1990; Johannesson et al., 1997, 2004, 2014; Leybourne and Johannesson, 2008; Shiller, 2010; Tang and Johannesson, 2010b; Willis and Johannesson, 2011; Gangloff et al., 2014; Guo et al., 2010; Steinmann and Stille, 2006, 2008; Stille et al., 2006). The unique chemical properties of trivalent Lewis acid REE include a systematic increase in ionic potential (valence normalized to ionic radius) with increasing atomic number (Z). Systematic variation in metal-ligand chemical reactivity makes the REE useful for studying biological impacts on

weathering in the earth's critical zone (NRC, 2001) because of the documented variation in their tendency to form stable complexes with organic and inorganic ligands common to natural waters (Wood, 1990; Byrne and Li, 1995; Davranche et al., 2004, 2005; Sonke and Salters, 2006; Pourret et al., 2007a,b; Pourret and Martinez, 2009; Yamamoto et al., 2010; Grybos et al., 2007). Hence their mobilization (i.e., chemical denudation) from a bioactive weathering profile and into stream drainage waters may be strongly influenced by incongruent weathering reactions and organic carbon flux (Dupre et al., 1999; Gruau et al., 2004; Pourret et al., 2010).

Aqueous geochemical signatures of streams vary with time because of dynamic mixing of waters from spatially distinct catchment locations (Nakajima and Terakado, 2003; Bailey et al., 2004; Voegelin et al., 2012) including biological "hot-spots" (McClain et al., 2003). Therefore, occurrences of REE-enriched discharge, and REE fractionation patterns may help to constrain the timing and spatial distribution of weathering in upland soils and to help resolve the temporal dynamics of catchment bio-

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weathering in particular (Dupre et al., 1999; Pourret et al., 2007a,b, 2010). To the extent that different critical zone water sources might be shown to produce distinct rare earth element and yttrium (REY) signatures and/or concentrations, as well as dynamic changes in the same over hydrologic events, we postulated that they may also be useful to resolving up-gradient biological weathering processes in natural catchments.

Variation in REY fractionation patterns during chemical denudation reflects their relative mobilities, in turn controlled by the formation of mobile aqueous complexes (organic and inorganic), as well as sorption and co-precipitation effects (Sonke and Salters, 2006; Pourret et al., 2007a; Laveuf and Cornu, 2009; Goyne et al., 2010). However, the impacts of DOM complexation on REY release during regolith weathering remain unclear. For example, DOM has been shown to be preferentially enriched in heavy REEs (HREE: Dy to Lu) because of their smaller ionic radii (the "lanthanide contraction effect") favoring incorporation into stable complexes with acidic organic functional groups (Sonke and Salters, 2006). Conversely, Davranche et al. (2011) reported middle (M)REE downward concavity patterns in soil solutions during wetland soil reduction, attributing to DOM a tendency to concentrate MREE. In either case, REY-ligand complexation affects non-stoichiometric dissolution of primary minerals (Goyne et al., 2010) and the effective solubilization and transport of complexed REY in natural waters (Xiong, 2011).

Because of their +3 charge, REEs are subject to adsorption at surfaces of secondary minerals (Bau, 1999; Bau and Koschinsky, 2009), and scavenging by Fe, Mn, and Al-(oxy)hydroxides during co-precipitation (Bau, 1999; Ohta and Kawabe, 2001). As a result of their high affinity for Mn-, Fe-(oxyhydr)oxides, REEs are postulated to also cycle in and out of soil pore waters during dissolution-precipitation via redox or non-redox derived mechanisms (Pokrovsky and Schott, 2002; Davranche et al., 2011), especially as pore waters fluctuate between supersaturated and undersaturated conditions with respect to REE-sorbing solid phases (Thompson et al., 2006b). In addition to dissolution-induced REE release, high specific surface area colloidal organo-mineral complexes are also mobilized during precipitation (e.g. rainfall) events. Pulsed colloidal (<1 μm particulate) dispersion or coagulation may result from wetting–drying events that promote excursions in pH or redox status driven by rapid microbial response. Prior experimental studies indicate that fluctuations in Eh/pH of natural soils induce colloidal dispersion that mobilizes nano-particles enriched in the lanthanide series metals (Viers et al., 1997; Braun et al., 1998; Thompson et al., 2006a, 2013). Redox conditions therefore likely influence REE fractionation through these multiple indirect mechanisms in soils and aquatic environments (Elderfield, 1988; Moffett, 1994; Bau and Koschinsky, 2009; Davranche et al., 2011).

Redox effects on REE fractionation can be direct as well, however, as europium and cerium are both redox sensitive. Eu deviates from the other REE in that it occurs in both (III) and (II) valence states. Reduction of Eu(III) requires strong reducing conditions rarely encountered in low pressure-temperature systems (Panahi et al., 2000; Laveuf and Cornu, 2009), but Eu(II) predominates in magmatic systems (Henderson, 1996), and bivalent Eu is introduced to the critical zone in primary tectosilicate minerals such as feldspars (K-feldspar and plagioclases), where it substitutes preferentially into Ca^{2+}, Na^+, and K^+ sites (Schnetzl and Philpott, 1970). Preferential dissolution of feldspars relative to other REE-bearing primary minerals should, therefore, result in positive aqueous Eu-anomalies (Ma et al., 2011; Brioschi et al., 2013).

Conversely, Ce occurs in (III) or (IV) valence states in soils and sediments. The oxidation of Ce(III) occurs at Eh values around 300 mV (De Carlo and Wen, 1998), a condition that is commonly encountered in sub-oxic to oxic surficial environments. This induces changes in ionic charge and radius that decouple Ce(IV) from the rest of the REE, commonly promoting its secondary solid phase incorporation, generating positive Ce anomalies in soils (Feng, 2010; Laveuf et al., 2012).

Given that radius- and redox-state-dependent fractionation of REY occur in low temperature geochemical systems, the current work sought to assess whether REY trends in rock, soil and natural water could be applied to resolve aspects of biogeochemical weathering resulting from snowmelt events in seasonally-snow covered nested catchments located in the JRB-CZO. The principal objectives were (i) to explore whether REY patterns of critical zone catchment sources are reflected in time dynamics of stream water REY efflux, including their changes with time and spatial scale and (ii) to reveal biogeochemical processes influencing catchment REY fractionation during snowmelt events. We postulated that pore and stream waters of the snowmelt period would contain useful REY signatures of biological weathering from the upland source areas.

2. Materials and methods

2.1. Study site

The field experimental design takes advantage of a nested headwater catchment infrastructure located in montane mixed conifer forests within the Jemez River Basin Critical Zone Observatory (JRB-CZO) (Brooks and Vivoni, 2008; Chorover et al., 2011) in the Valles Caldera National Preserve, northern New Mexico (Fig. 1A). The JRB-CZO is instrumented to monitor CZ processes including fluid (gas, water and solute) flows from pedon to catchment scales (Fig. 1, also see http://criticalzone.org/catalina-jemez/). Instrumented pedon sites were located within a zero order basin (ZOB) (Fig. 1D) on Redondo Dome (35°52′56″N, 106°32′8″W) within the larger La Jara catchment (LJC, Fig. 1C). The ZOB is south-oriented with dominant SW and SE facing slopes like most of the larger East Fork Jemez watershed (EFJW, Fig. 1B). Most of Redondo Dome, including the ZOB, is underlain by Pleistocene aged rhyolitic volcaniclastics of the Tewa Group (http://geoinfo.nmt.edu/publications/maps/geologic/ofgm/). The bedrock within the ZOB is comprised of a combination of dense, highly fractured porphyritic rhyodacite that underlies 45–50% of the ZOB, and partially welded and hydrothermally altered Bandelier Tuff that occupies the other 50–55%. The rhyodacite mineral composition includes 25–30% quartz, 40–45% plagioclase feldspar (albite and oligoclase), and 25–30% alkali feldspar (sanidine) with a density near 2.6 g/cm³, whereas the Bandelier Tuff composition can be more variable depending on degree of hydrothermal alteration. The tuff sampled from the ZOB exhibited a mineral composition of (on a mass basis) 40–45% quartz, 20–30% plagioclase feldspar, 5–10% alkali feldspar, 5–10% smectite, and 2–5% zeolite, where the zeolite and smectite represent hydrothermal alteration products. ZOB soils are classified as Mollisols and Alfisols. Catchment and hydrometeorological properties for ZOB, LJC, and EFJW are included in Tables 1 and 2.

Most of the precipitation in the site occurs during the winter season and, at higher elevations, primarily as snow. According to prior studies in the East Fork Jemez watershed (Porter, 2012; Perdrial et al., 2014a), snowmelt is the dominant source of "deep" groundwater recharge, as is common in western montane regions (Bales et al., 2006). In this study site, infiltrating snowmelt transports a large seasonal pulse of organic carbon through soil profiles (Perdrial et al., 2012) and into surface water (Perdrial et al., 2014a). Fluorescence spectroscopy studies of DOM in JRB-CZO soils indicate that they comprise a mixture of plant-derived polyphenols, as well as microbial polysaccharides and proteins, with the ratio of plant versus microbial fluorescent components showing seasonal and sorption–desorption dependence (Perdrial et al., 2014a; Vazquez-Ortega et al., 2014).

2.2. Sample collection

Rock samples of porphyritic rhyodacite and zeolitilized Bandelier Tuff were collected in summer 2010 around Redondo Dome in order to span the range of lithologic variation. Soil samples obtained from