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Solid-phase redistribution of rare earth elements in hillslope pedons subjected to different hydrologic fluxes

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ABSTRACT

Prior studies indicate that patterns of rare earth element (REE) depletion or enrichment in critical zone (CZ) weathering systems are sensitive to variation not only in lithology, but also in climatic and/or biological processes. Organic ligands and secondary mineral surfaces vary in complex stability with different lanthanide series metals, which can result in solid-solution fractionation during incongruent mineral dissolution. REE fractionation during precipitation of solid phase weathering products is also expected to vary with host phase affinity and aqueous geochemistry along fluid flow paths. We postulated that patterns of REE fractionation during pedogenic weathering would exhibit mass-dependent trends as a function of depth in the soil profile. We further hypothesized that REE signatures would be influenced by depth-dependent variation in water and dissolved organic carbon (DOC) fluxes resulting from topographic position of the pedon under investigation. Field-based hypothesis testing utilized instrumented pedons derived from rhyolitic bedrock overlain by mixed conifer forest in the Jemez River Basin Critical Zone Observatory (JRB-CZO). REE depletion trends correlated with topographically-induced variation in soil pore water and DOC through-fluxes occurring predominantly during winter snowmelt. Bulk regolith analyses indicated that light rare earth elements (LREE) were depleted preferentially relative to medium and heavy REE (MREE and HREE). Lateral fluxes of water and DOC through subsurface horizons in the concave hillslope pedon correlated not only with greater REE depletion, but also with greater fractionation of REE into organo-metal colloid forms (2–23%) relative to a planar site hillslope pedon (3–13%) where vertical water and DOC fluxes were predominant. MREEs were preferentially retained in secondary colloids, indicating a mechanism for their stabilization in the weathering profile. Positive Ce-anomalies in the soils were the result of Ce retention in pedogenic Fe-(oxy)hydroxides.

1. Introduction

The lanthanide series of rare earth elements (REE, atomic numbers 53 through 71) is characterized by systematic variation in atomic mass, ionic radius, and electron configuration, as well as variation in oxidation state (Bau et al., 1995; Bau, 1999; Ohta and Kawabe, 2001; Davranche et al., 2004, 2011; Pourret et al., 2007b; Bau and Koschinsky, 2009). Fractionation behavior of the rare earth elements and yttrium (REY, the latter being included because of similar primary mineral sourcing and chemical reactivity as the lanthanides) has been used to elucidate soil and sediment biogeochemical weathering processes such as mineral dissolution, argilluviation, redox fluctuations, and biological cycling among others (Ronov et al., 1967; Cullers et al., 1975; Aubert et al., 2001, 2002; Coppin et al., 2002; Stille et al., 2006a, b, 2009; Nezat et al., 2007; Leybourne and Johannesson, 2008; Shiller, 2010; Tang and Johannesson, 2003, 2010a,b; Ma et al., 2011; Willis and Johannesson, 2011; Brioschi et al., 2013; Gangloff et al., 2014).

Systematic variation in chemical properties across the REY (e.g., the lanthanide contraction effect) (Sonke and Salters, 2006) leads to series wide trends in incorporation into (or exclusion from) secondary minerals and/or complexes with organic and inorganic ligands The variation also makes them appropriate for studies of biogeochemical weathering and fractionation during biogeochemical denudation of regolith (Elderfield, 1988; Elderfield et al., 1990; Wood, 1990; Sholkovitz,

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Abbreviations: Ce/Ce*, cerium anomaly; CZ, critical zone; DOC, dissolved organic carbon; DOM, dissolved organic matter; Eu/Eu*, europium anomaly; HREE, heavy rare earth elements; JRB-CZO, Jemez River Basin Critical Zone Observatory; LREE, light rare earth elements; LRO, long range order; MC, mixed conifer; MREE, medium rare earth elements; OC, organic carbon; PCap, passive capillary sampler; REE, rare earth elements; REY, rare earth elements and yttrium; SE, sequential extraction; SOM, soil organic matter; SRO, short range order; TWI, topographic wetness index; UCC, upper continental crustal; WY, water years; ZOB, zero order basin.

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1992; Johannesson et al., 1997). Chemical reactions with soluble ligands, soil organic matter, layer silicate clays, Fe, Mn, and Al-(oxy)hydroxides, as well as variations in redox status have all been reported to influence REY fractionation, transport, and fate in soils and natural waters (Goldberg et al., 1963; Cullers et al., 1975; Viers et al., 1997; DeBaar et al., 1988; Elderfield, 1988; Nakajima and Terakado, 2003; Pourret et al., 2007b; Steinmann and Stille, 2008; Laveuf et al., 2008, 2012; Laveuf and Cornu, 2009; Goyne et al., 2010; Guo et al., 2010b; Johannesson et al., 2014).

The current study investigates partitioning of REY between mobile porewaters (predominantly snowmelt-derived) and residual soils originated from rhyolitic bedrock. We sought to evaluate the extent to which lanthanide series fractionation patterns, Y/Ho divergence, and Ce anomalies can be used to quantify the relative contributions of “biological weathering”, as reflected in organic ligand-promoted REY fractionation between mobile fluids and weathering residuum. We postulated that ‘bio-inorganic’ solid phase products of similar lability (as measured by kinetic metal dissolution during sequential aqueous chemical extraction) will contain specific REY signatures denoting their pedogenic origin. In particular, we are interested in probing how REY signatures change as one moves from the complex of exchangeable cations, into organo-mineral colloids, and across a range of metal (oxy)hydroxide crystallinity. These same solid phase products form stable hetero-aggregates of mineral and organic matter. Therefore, it was of interest to determine whether mineral-stabilized organic matter with relatively long turnover times (e.g., see Torn et al., 1997; Mikutta et al., 2012) contains specific REY signatures. Thus, such signatures translocated episodically into surface waters could signal organic matter destabilization.

In the Jemez River Basin Critical Zone Observatory (JRB-CZO) infiltrating snowmelt transports a large seasonal pulse of soluble organic carbon through instrumented pedons (Perdrial et al., 2012, 2014a; Vázquez-Ortega et al., 2015). Infrared and fluorescence spectroscopy studies of the dissolved organic matter (DOM) in JRB-CZO soils indicated 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; Vázquez-Ortega et al., 2014). We previously showed that total REY concentrations in effluent waters across a range of nested, instrumented catchment scales – hillslope to catchment to watershed – were strongly controlled by DOC concentration, and exhibited similar REY/DOC mass ratios (Vázquez-Ortega et al., 2015). Furthermore, soils distributed in different landscape positions contributing to catchment REY effluxes exhibited distinct depth-dependent chemical depletion patterns and an increase in the magnitude of positive Ce-anomalies with depth (preferential accumulation of Ce in deeper horizons with respect to host lithologies). Those results led to the further specific hypotheses tested in the current work: (i) REY depletion patterns reflect landscape-location-specific patterns of water and organic carbon flux observed at the sub-pedon scale; (ii) Ce is preferentially accumulated in lower horizons by adsorption and/or co-precipitation with Fe-(oxy)hydroxide minerals; and (iii) depth dependent trends in Y/Ho ratio reflect differential incorporation of these elements in pedogenic Fe-(oxy)hydroxide precipitates (e.g., Bau, 1999; Thompson et al., 2013) despite the fact that no systematic variations in Y/Ho ratios were observed in bulk soils.

As a result, the principal objective of the present study was to quantify mineral and organic phases controlling the retention of REY as a function of depth in pedons located in three distinct landscape positions (planar, convex, and concave) within a single zero order basin. A sequential chemical extraction procedure was performed to quantify the mass fraction of REY incorporated into adsorbed versus co-precipitated secondary species including Mn-oxides (e.g., birnessite), organo-metal colloids, short range order (SRO) Fe-oxides (e.g., ferrihydrite), long range order (LRO) Fe-oxides, (e.g., goethite), and residual materials (Land et al., 1999; Laveuf et al., 2012).

2. Materials and methods

2.1. Study site and sample collection

The study utilized data and samples obtained from six instrumented pedons under mixed conifer (MC) forest in a 0.15 km^2 zero order basin (ZOB) of the La Jara catchment that is part of the East Fork Jemez River watershed within the Valles Caldera National Preserve, NM (Fig. 1). The ZOB has a south-facing orientation with dominant SW and SE facing slopes separated by a concave swale that displays negligible surface flows outside of high discharge events and then only at the ZOB outlet (flume location, Fig. 1). The instrumented ZOB is the focus of inter-disciplinary surface earth process studies within the JRB-CZO (NRC, 2001; Brooks and Vivoni, 2008; Chorover et al., 2011; Vázquez-Ortega et al., 2015). Soils are established on Pleistocene aged rhyolitic volcaniclastic parent materials. Bedrock comprises a mixture of fine-grained porphyritic rhyodacite and hydrothermally altered Bandelier Tuff (http://geoinfo.nmt.edu/publications/maps/geologic/ofgm/). Parent materials were impacted by alkaline hydrothermal alteration soon after caldera collapse yielding transformation of volcanic glass dominantly to smectite with some zeolite (Goff and Gardner, 1988; Chipera et al., 2008). Outcrop samples of the parent rocks were collected in summer 2010 around Redondo Dome spanning the range of lithologic variation. Soils are derived from rhyolitic bedrock and tuff (Perdrial et al., 2012; Vázquez-Ortega et al., 2015). Soil solid samples were obtained from Pedon 1 (planar), Pedon 3 (convex), and Pedon 5 (concave) hillslope profiles, all excavated at the time of sampler installations (September, 2010). Soil samples were collected by genetic horizon, sealed in zip-lock bags and stored at 4 °C. Upon return to the lab, soil samples were air dried, sieved to recover the <2 mm fraction, homogenized, and stored at room temperature prior to further chemical analysis.

The six MC ZOB pedons were instrumented with in situ passive capillary soil solution (i.e., “PCap” or “wick”) samplers that have been shown effective for REY and DOC pore water chemistry sampling (Holder et al., 1991; Biddle et al., 1995; Perdrial et al., 2012, 2014b) at 10, 30 and 60 cm depths. Flux values for DOC and REY were determined as the product of solution mass and molality for each sampling date, summing these products across all sampling dates per water year, and normalizing the result to the cross-sectional area of the wick sampler plate (0.09 m^2). Porewater samples were filtered through combusted 0.7 μm glass fiber filters (GF/F, Whatman, Alameda Chemical & Scientific Inc., Oakland, CA) for DOC and through 0.45 μm nylon filters (Millipore, Thermo Fisher Scientific) for metals, into separate acid washed HDPE bottles and transported under refrigerations (~4 °C) to the laboratory within a maximum of 2 d after sampling. All soil solutions included in this study were collected during the water years (WY) of 2011, 2012 and 2013. Water years are defined as October 1 to September 30.

2.2. Solid phase characterization

Bulk soil samples and parent materials (porphyritic rhyodacite and altered Bandelier Tuff) were analyzed for total elemental composition by lithium metaborate/tetraborate fusion followed dissolution of the pellet in nitric acid and solution phase analysis by inductively coupled plasma (ICP) optical emission spectrometry (-OES) and mass spectrometry (-MS) (Activation Laboratories, Ancaster, Ontario). Recovery of REY for certified standards W-2a (U.S. Geological Survey mafic rock reference) and NCS DC70009 (tungsten ore) were in the range of 95–105% and 94–104%, respectively. Total organic carbon in the bulk solid samples was determined by high temperature oxidation followed by infrared detection of CO_2 using a Shimadzu TOC-VCSH system equipped with a solid sample module SSM-5000A (Columbia, MD). Organic C, P, Mn, and Fe concentrations in bulk soil for the planar, convex, and concave hillslope profiles located in the La Jara ZOB are included in Table 1.