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Trace element mobilization during incipient bioweathering of four rock types

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Abstract

Lithogenic trace element (TE) patterns of distribution, fate, and behavior in soils are influenced by plants and microorganisms. Our controlled mesocosm experiments quantified how incipient weathering of mineral-bound TEs (Be, V, Sr, Ba, Cr, Co, Ni, Mo, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, Tl, and Pb) varies across four porous mineral substrates (basalt, rhyolite, granite, and schist), in the presence of buffalo grass (*Bouteloua dactyloides*), associated bacteria, and arbuscular mycorrhizal fungi (AM), a common plant symbiont. Particular focus was given to the net transfer of elements between the solid and solution phases, including chemical denudation (loss of element from the rock to the solution), plant TE uptake, and total mobilization (sum of denudation loss and uptake into plant biomass).

Results revealed differences in TE denudation among rocks, basalt having the highest loss and schist the lowest. TE leaching in solution was time-dependent and it was likely influenced by variations in pH and DOC that were rock- and treatment-specific. The element with the highest rock-normalized release to the solution and highest enrichment in plant biomass was Mo across all rocks. Plants decreased denudation loss compared to abiotic controls for a large number of TEs in all substrates due to plant uptake, but for some elements increase in weathering due to plant activity resulted in increased denudation. Differences in TE patterns of behavior could be related to their Goldschmidt groups. Plant uptake was controlled by TE availability in solution, as well as plant physiological requirements. Plants and associated microbiota significantly enhanced mobilization for the majority of TEs across all rocks.

Mycorrhiza significantly increased above-ground plant biomass production in rhyolite and concentrations in plant tissues for a high number of TEs in basalt. TE uptake into biomass was positively correlated with percent mycorrhizal infection, particularly in basalt and rhyolite. Mycorrhizal fungi also influenced TE denudation, rock-water fractionation, and total mobilization according to the rock type. Mycorrhizal activity was associated with a significant decrease in pH and increase in DOC fluxes in schist, supporting the idea that fungi enhance production of root exudates especially in substrates that are difficult to weather.

Our results highlight the importance of incipient weathering at the plant-rock interface for patterns of TE cycling. They also indicate the importance of mycorrhiza in mineral dissolution, TE denudation, plant element uptake, and biomass growth.

Keywords: Buffalo grass; Arbuscular mycorrhiza; Weathering; Trace elements biogeochemistry; Basalt; Rhyolite; Granite; Schist; Dissolved organic carbon

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1. INTRODUCTION

Incipient soil formation initiates the development of a key climate- and nutrient-regulating compartment of the biosphere (McClain et al., 2003; Young and Crawford, 2004). Biological activities in the soil – such as plant fixation of reduced carbon, root and microbial exudation, and overall biotic colonization of porous geomedia – impact many ecosystem processes, including carbon sequestration and nutrient/metal cycling through weathering processes (Drever, 1994). Rock weathering results in the release of major and trace elements (TEs) into solution, where they may be subjected to plant uptake, precipitation into neoformed minerals, adsorption to surfaces, or leaching (Kabata-Pendias and Pendias, 1992; Prasad et al., 2005; Hooda, 2010). Trace elements, which exhibit a wide range of inorganic and organic ligand affinities, may be differentially partitioned in solution in the presence or absence of biota. The distribution of lithogenic elements among product phases may also depend on – and therefore potentially provide a signature of – biological activity. While mineral exposure to water, temperature variation, and oxidative conditions result in weathering reactions including dissolution and precipitation of minerals, plants and microbes exert strong controls over these processes particularly as a result of carbon fixation and cycling (Calvaruso et al., 2006). Activities of plants and microbes are expected, therefore, to alter the rate and trajectory of primary to secondary mineral weathering, which feeds back to affect other key element cycles, e.g., carbon through stabilization of organic (or inorganic) residues on reactive secondary mineral surfaces and their aggregates (Chorover, 2012). The resulting soil structure has impacts that extend into the ecosystem along the food chains, through its influence on ecosystem structure and stability (Osterkamp and Hupp, 2010).

Many lab and field studies have tried to quantify plants' role in mineral weathering, element cycling, and soil formation, and several have stressed the importance of associative interactions with microorganisms (Banfield and Nealson, 1997; Berner et al., 2003; Taylor et al., 2009). Fueled by the geochemical disequilibrium that characterizes the Earth's critical zone, including that of plant-derived photosynthetic inputs, microbes are major drivers of lithogenic and bioactive element cycles on the land surface, contributing significantly to element release, bioavailability control, and transfer from minerals to higher plants (Calvaruso et al., 2006; Balogh-Brunstad et al., 2008). Microbial contributions to weathering have been reported for a wide range of mineral types including metal oxides, phosphates, carbonates and silicates (Hinsinger and Gilkes, 1997; Moulton et al., 2000; Hinsinger et al., 2001; Lian et al., 2008; Akter and Akagi, 2010). In addition to promoting primary mineral dissolution through the production of complexing ligands and affecting pH, coupled plant and microbial activity may control the molecular structure of secondary minerals formed during incongruent primary silicate weathering. It is known that microbes alter the rates and trajectories of mineral nucleation and crystal growth through both passive and active biomineralization mechanisms (Konhauser, 2006). A number of studies have addressed the coupling of plant and bacteria with fresh rock substrates weathering (Bashan et al., 2002, 2006; Puente et al., 2004, 2009; Calvaruso et al., 2006; Lopez et al., 2009; Uroz et al., 2009, 2011; Calvaruso et al., 2013).

Mycorrhizal fungi have been shown to play an essential role in weathering processes and plant nutrition (Van Breemen et al., 2000; Wallander and Gadd, 2006; Leake et al., 2008; Van Schöll et al., 2008; Andrews et al., 2011; Bonneville et al., 2011; Quirk et al., 2012; Remiszewski et al., 2016). The small diameter of fungal hyphae and the capacity to extend rapidly and explore a large volume of soil beyond the rooting zone (Leake et al., 2004) make mycorrhizal fungi particularly effective in dissolving primary mineral structures to obtain limiting nutrients such as P and K (Blum et al., 2002; Asghari and Cavagnaro, 2012). In low nutrient environments, mycorrhizal plants may increase nutrient uptake, either directly from the soil by extraradical hyphae and subsequent translocation to the plant, or by mycorrhizal effects on root activity. Mycorrhiza can modify the physicochemical environment of the root by releasing own exudates (Rillig and Steinberg, 2002; Hoffland et al., 2004) and/or enhancing the production of root exudates that contribute to primary mineral dissolution (Marschner et al., 1986, 1997; Hinsinger, 1998; Taylor et al., 2009; Schmalenberger et al., 2015). Plant root exudates consist of a complex mixture of organic acid anions, phytosiderophores, sugars, vitamins, amino acids, purines, nucleosides, inorganic ions (e.g. HCO_3^-, OH^-, H^+), gaseous molecules (CO_2, H_2), and enzymes, which are effective in promoting mineral dissolution and nutrient acquisition required for plant growth (Dakora and Phillips, 2002). While effects of ectomycorrhizal fungi on weathering and lithogenic nutrient uptake have been more often approached (Landeweert et al., 2001; Bonneville et al., 2009; Smits et al., 2012; Schmalenberger et al., 2015), less work has been done with arbuscular mycorrhiza (AM). Effects of AM on rock weathering remain elusive (Bashan et al., 2007; Koele et al., 2014; Thorley et al., 2015; Remiszewski et al., 2016), particularly their impacts on geochemical transformations in fresh rock environments, during incipient soil formation (Hoffland et al., 2004; Zaharescu et al., 2017). Whereas major element denudation in solution closely reflects major mineralogical transformations during weathering (Burghelea et al., 2015), TE partitioning is sensitive to specific mechanisms driving weathering reactions, including bio-ligand effects (Gobran and Huang, 2005; Goyne et al., 2010; Thompson et al. 2013; Vazquez-Ortega et al., 2015). TEs are hard or soft Lewis basis, which has a direct bearing on their potential for formation of the complexes in solution, and therefore their weathering, plant uptake, and mobility. Thus, examining TE cycling in rock weathering systems has the potential to provide novel insights into the geochemical role of biota in early soil formation. This is due, in part, to systematic variation in TE reactivity toward organic ligands or secondary phase precipitates, reflected in both dissolution and nucleation reactions that control TE mobility and availability. Many TEs are essential micronutrients for microbial and plant uptake, but too much of an increase in their concentrations can pose a serious threat to the