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Ca, Sr and Ba stable isotopes reveal the fate of soil nutrients along a tropical climosequence in Hawaii

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ABSTRACT

Nutrient biolifting is an important pedogenic process in which plant roots obtain inorganic nutrients such as phosphorus (P) and calcium (Ca) from minerals at depth and concentrate those nutrients at the surface. Here we use soil chemistry and stable isotopes of the alkaline earth elements Ca, strontium (Sr) and barium (Ba) to test the hypothesis that biolifting of P has been an important pedogenic process across a soil climosequence developed on volcanic deposits at Kohala Mountain, Hawaii. The geochemical linkage between these elements is revealed as generally positive site-specific relationships in soil mass gains and losses, particularly for P, Ba and Ca, using the ratio of immobile elements titanium and niobium (Ti/Nb) to link individual soil samples to a restricted compositional range of the chemically and isotopically diverse volcanic parent materials. At sites where P is enriched in surface soils relative to abundances in deeper soils, the isotope compositions of exchangeable Ca, Sr and Ba in the shallowest soil horizons ($<$10 cm depth) are lighter than those of the volcanic parent materials and trend toward those of plants growing on fresh volcanic deposits. In contrast the isotope composition of exchangeable Ba in deeper soil horizons ($>$10 cm depth) at those sites is consistently heavier than the volcanic parent materials. The isotope compositions of exchangeable Ca and Sr trend toward heavier compositions with depth more gradually, reflecting increasing leakiness from these soils in the order Ba $<$ Sr $<$Ca and downward transfer of light biocycled Ca and Sr to deeper exchange sites. Given the long-term stability of ecosystem properties at the sites where P is enriched in surface soils, a simple box model demonstrates that persistence of isotopically light exchangeable Ca, Sr and Ba in the shallowest soil horizons requires that the uptake flux to plants from those near-surface layers is less than the recycling flux returned to the surface as litterfall. This observation implicates an uptake flux from an additional source which we attribute to biolifting. We view the heavy exchangeable Ba relative to soil parent values in deeper soils at sites where P is enriched in surface soils, and indeed at all but the wettest site across the climosequence, to represent the complement of an isotopically light Ba fraction removed from these soils by plant roots consistent with the biolifting hypothesis. We further suggest that decreasing heaviness of depth-integrated exchangeable Ba in deeper soils with increasing median annual precipitation across the climosequence reflects greater reliance on shallow nutrient sources as site water balance increases. While the Ca, Sr and Ba isotopes considered together were useful in confirming an important role for nutrient biolifting across the climosequence, the Ba isotopes provided the most robust tracer of biolifting and have the greatest potential to find application as an isotopic proxy for P dynamics in soils.

1. Introduction

The role of plants in promoting mineral and rock weathering and the strategies that plants use to obtain and sequester inorganic rock-derived nutrients are central themes in the rapidly evolving study of Earth's Critical Zone. A useful conceptual framework that links inorganic nutrient uptake by plants to rock weathering is termed “biolifting”, a pedogenic process which results in relative depletion of nutrient elements such as phosphorus (P) or calcium (Ca) in deeper soil horizons and the enrichment of those elements in near-surface organic-rich horizons making use of the plant rooting network as the uptake pathway (Jobbagy and Jackson, 2001). It is likely that biolifting plays an important role in stimulating weathering in the subsurface by reinforcing strong ionic gradients between solid and liquid phases (Kelly et al., 1998).

While evidence for biolifting has been reported in numerous soil systems, the ability to convincingly demonstrate biolifting is complicated by the fact that other processes such as deposition of aerosols and dust can also enrich surface horizons with inorganic “rock-derived”

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nutrients (Derry and Chadwick, 2007). Distinguishing between these two (and other) processes may be possible by exploring differences in the isotope composition of biolifted vs. atmospherically-deposited nutrients. The isotope ratio approach for distinguishing nutrient sources may be applicable when considering nutrients such as Ca that have either multiple stable isotopes (Wiegand et al., 2005) or a radiogenic isotope component (Farkaš et al., 2011). For example Ca stable isotope ratios (e.g. $^{44/40}$Ca, uncorrected for mass dependent isotope fractionation) have been increasingly used to directly assess sources of and processes affecting Ca in environmental systems (Fantle and Tipper, 2014). Calcium radiogenic isotope ratios (e.g. $^{44/40}$Ca, corrected for mass dependent isotope fractionation) have likewise found application at sites where potassium-rich rocks having sufficient age to have developed a radiogenic Ca component are prevalent (Farkaš et al., 2011). Moreover, the radiogenic strontium (Sr) isotope system ($^{87/86}$Sr) has been widely used as a proxy tracer for Ca particularly at sites where there is both an isotope gradient of plant-available Sr down the soil profile and a Sr isotope contrast between soil and bedrock minerals and atmospheric deposition (e.g. Bullen and Bailey, 2005). However the isotope ratio approach is obviously not applicable for mono-isotopic nutrients such as P and thus the use of proxy isotope tracers is required.

Metal stable isotopes are increasingly helping Earth scientists understand weathering, hydrologic and biologic processes related to pedogenesis by providing unique perspectives on the sources of metals and mechanisms determining their distribution in soils (Bullen, 2013). Studies of soils using the isotopes of metals such as lithium (Rudnick et al., 2004), magnesium (Tipper et al., 2010), calcium (Wiegand et al., 2005) and iron (Thompson et al., 2007) are becoming more common. While these four isotope systems have increasingly provided new insights into aspects such as paleohydrology, redox status, weathering intensity and nutrient cycling, there remain several largely unexplored stable isotope systems such as Sr and barium (Ba) that may serve as useful proxy tracers. Here we develop a Ca–Sr–Ba stable isotope approach to support our working hypothesis that biolifting of P has been an important pedogenic process along a well-characterized arid-to-humid climosequence developed on volcanic rocks on Kohala Mountain, Hawaii (Chadwick et al., 2003; Vitousek and Chadwick, 2013). We propose that broad similarities in depletion and enrichment patterns of these alkaline earth elements to those of P in soils where P is enriched in surface soils relative to abundances in deeper soils suggests that their stable isotope systematics ($^{44/40}$Ca, $^{88/86}$Sr, $^{138/134}$Ba) are especially useful in providing proxies for P biodynamics in these soils.

Previous studies have shown that plants preferentially take up the light isotopes of Ca (e.g. Page et al., 2008; Hindshaw et al., 2011), Sr (deSouza et al., 2010) and Ba (Bullen et al., 2012) and thus isotope compositions in surface soil horizons that are lighter than rock substrates can indicate biological processing and accumulation of these elements as a cycling mechanism. In contrast, atmospherically-sourced cations may be isotopically heavier than rocks particularly in near-coastal areas where the characteristically heavy Ca (Zhu and Macdougall, 1998), Sr (Fietzke and Eisenhauer, 2006) and Ba (Horner et al., 2015) of seawater can influence aerosol composition. Wiegand et al. (2005), in their study of Ca isotope variability across a soil chronosequence developed on basalt and representing four million years of weathering in the Hawaiian Islands, demonstrated that young soils have exchangeable Ca that is lighter than Ca in the fresh basalt due to recycling of light Ca in litterfall. They proposed that the observed increase in $^{44/40}$Ca of exchangeable Ca with increasing soil age resulted from increasing exposure to seawater Ca-dominated aerosols. On the other hand Holmden and Belanger (2010), in their study of Ca isotope systematics at a boreal forest setting in Canada, found that rock weathering- and atmospherically-sourced Ca were essentially identical in Ca isotope composition. They proposed that heavier Ca in soil water compared to that in rock and atmospheric sources resulted from greater uptake flux of Ca by plants relative to the recycling flux of Ca to soil via litterfall decomposition. Interpretation of the Ca isotope composition of soil pools must additionally consider the role of inorganic processes such as secondary mineral formation (e.g. precipitation of calcium carbonate) as demonstrated by Tipper et al. (2006) in their study of a Himalayan catchment.

While Ca stable isotopes have been widely used to study weathering processes, plant nutrition strategies and pedogenesis, stable isotopes of Sr and Ba have only been minimally utilized. In an early study Halicz et al. (2008) found that terra rosa soil of eolian origin in the Judea Mountains and speleothems formed in an underlying cave fed by drainage through the soils had significantly lighter Sr compared to the carbonates that host the cave system. More recently Shalev et al. (2013) studied soil leaching along a rainfall gradient in Israel and found decreasing whole-soil $^{88/86}$Sr with increasing Al-clay content and extent of leaching. These two studies suggest that Sr (and perhaps neighboring alkaline earth elements Ca and Ba) may become lighter in residual soils due to progressive weathering and leaching of an isotopically heavy fraction to weathering solutions. Of the few existing studies on low-temperature applications of Ba isotopes, Bullen et al. (2012) reported initial results for a hydropedologic study of a northern hardwood forest showing that plants have significantly lighter Ba than the underlying mineral soils and that biocycled Ba concentrates in the forest floor, similar to patterns observed for Ca and Sr stable isotopes at that site. In a pertinent experimental study Von Allmen et al. (2010) showed that $BaCO_3$ and $BaSO_4$ precipitated from solution contain lighter Ba than remaining dissolved Ba, similar to the isotope fractionation behavior for Ca and Sr in carbonates and sulfates. This latter result provides a plausible mechanism to account for the observed heavy composition of Ba in seawater relative to that of rocks (Horner et al., 2015) given that the Ba concentration of seawater is largely controlled by precipitation of barite in the water column (Gonneea and Paytan, 2006).

The main focus of this study was to test whether the Ca, Sr and Ba isotope compositions of the soil exchange pool can be used to understand processes influencing soil development (e.g. chemical weathering, secondary mineral formation, atmospheric deposition, hydrologic transport) and particularly as a novel approach to assess the role of nutrient biolifting during pedogenesis along the Kohala climosequence. In this setting, P is a key indicator of soil nutrient status (Porder and Chadwick, 2009; Vitousek et al., 2010) and thus our goal was to identify linkages between P and these alkaline earth elements. We focused on the soil exchange pool as an integrated record of processes that influence the composition of soil water (e.g. Mulder and Cresser, 1994) and based our approach on the results of recent efforts to model and interpret the Ca isotope composition of soil exchange pools elsewhere (Holmden and Belanger, 2010; Fantle and Tipper, 2014). We used the isotopes to identify pedogenic processes, including biolifting of nutrients and their proxies, which have occurred across the climosequence in order to evaluate the interplay of mineral weathering, atmospheric deposition and plant nutrient uptake and recycling. We anticipated that the isotope systematics of Ca, Sr and Ba would differ systematically in that they exhibit a gradient of (bio)geochemical behavior due to differences in ionic radius which determines their site preference in minerals (e.g. Heijligers et al., 1979), sorption potential (e.g. Nesbitt et al., 1980) and roles in plant nutrition and toxicity (e.g. Smith, 1971; Lawrey, 1979).

As part of this study we documented unanticipated variability in Ca, Sr and Ba isotope compositions of the volcanic parent materials of these soils which provided a novel constraint on the assessment of isotope distribution in the soil exchange pool. In addition, we found that the ratio of titanium to niobium (Ti/Nb) in these volcanic deposits effectively characterizes magmatic evolution and geochemical variation across the spectrum of compositions. Because Ti and Nb are immobile elements in the Kohala soils, the Ti/Nb ratio was useful for linking individual soil samples to specific parent compositions which aided calculation and correlation of Ca, Sr, Ba and P mass transfers during pedogenesis.