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.

Keywords: isotopes; strontium isotopes; barium isotopes; nutrient biolifting; soil climosequence; soil exchangeable fraction; Andisols

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” 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 (Farkas et al., 2011). For example Ca stable isotope ratios (e.g. $^{44/40}\text{Ca}$, 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. $^{44/40}\text{Ca}$, 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 (Farkas et al, 2011). Moreover, the radiogenic strontium (Sr) isotope system ($^{87/86}\text{Sr}$) 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

69 obviously not applicable for mono-isotopic nutrients such as P and thus the use of proxy isotope
70 tracers is required.

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

87 Previous studies have shown that plants preferentially take up the light isotopes of Ca (e.g. Page
88 et al., 2008; Hindshaw et al., 2011), Sr (deSouza et al., 2010) and Ba (Bullen et al., 2012) and thus
89 isotope compositions in surface soil horizons that are lighter than rock substrates can indicate
90 biological processing and accumulation of these elements as a cycling mechanism. In contrast,
91 atmospherically-sourced cations may be isotopically heavier than rocks particularly in near-coastal

92 areas where the characteristically heavy Ca (Zhu and Macdougall, 1998), Sr (Fietzke and
93 Eisenhauer, 2006) and Ba (Horner et al., 2015) of seawater can influence aerosol composition.
94 Wiegand et al. (2005), in their study of Ca isotope variability across a soil chronosequence
95 developed on basalt and representing four million years of weathering in the Hawaiian Islands,
96 demonstrated that young soils have exchangeable Ca that is lighter than Ca in the fresh basalt due
97 to recycling of light Ca in litterfall. They proposed that the observed increase in $^{44/40}\text{Ca}$ of
98 exchangeable Ca with increasing soil age resulted from increasing exposure to seawater Ca-
99 dominated aerosols. On the other hand Holmden and Belanger (2010), in their study of Ca isotope
100 systematics at a boreal forest setting in Canada, found that rock weathering- and atmospherically-
101 sourced Ca were essentially identical in Ca isotope composition. They proposed that heavier Ca in
102 soil water compared to that in rock and atmospheric sources resulted from greater uptake flux of
103 Ca by plants relative to the recycling flux of Ca to soil via litterfall decomposition. Interpretation
104 of the Ca isotope composition of soil pools must additionally consider the role of inorganic
105 processes such as secondary mineral formation (e.g. precipitation of calcium carbonate) as
106 demonstrated by Tipper et al. (2006) in their study of a Himalayan catchment.

107 While Ca stable isotopes have been widely used to study weathering processes, plant nutrition
108 strategies and pedogenesis, stable isotopes of Sr and Ba have only been minimally utilized. In an
109 early study Halicz et al. (2008) found that terra rosa soil of eolian origin in the Judea Mountains
110 and speleothems formed in an underlying cave fed by drainage through the soils had significantly
111 lighter Sr compared to the carbonates that host the cave system. More recently Shalev et al. (2013)
112 studied soil leaching along a rainfall gradient in Israel and found decreasing whole-soil $^{88/86}\text{Sr}$ with
113 increasing Al-clay content and extent of leaching. These two studies suggest that Sr (and perhaps
114 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 hydrogeologic 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 (Cao et al., 2015; 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.

2. Site description

The Kohala soil climosequence is situated on the western limb of Kohala Mountain (Figure 1), the oldest of five shield volcanoes on the island of Hawaii, and is developed on 0.23 to 0.12 Ma Hawi Volcanic Series (HVS) alkalic cap lavas and ash. As reported by Spengler and Garcia (1986) these volcanic deposits are predominantly hawaiite (SiO_2 ~48-50wt.%) but range in composition through mugearite (SiO_2 ~52-55wt.%) to trachyte (SiO_2 ~58wt.%). The soils along the climosequence are developed on composites of HVS a`a lavas and tephra with emplacement of the latter post-dating the flows by a relatively small period of time (Chadwick et al., 2003). Details of geomorphology and soil landscape, soil ages, climate and paleoclimate, vegetation, water balance

and procedures for collecting soil samples used for this study are given elsewhere (Chadwick et al., 2003).

The major climatic variable is median annual precipitation (MAP), which varies from 200 mm near the coast to >4000 mm near the mountain crest. With increasing elevation and MAP along this climosequence a series of soil process domains are separated by pedogenic thresholds as described in Vitousek and Chadwick (2013). For MAP <~700 mm, while the <2-mm soil fractions have experienced significant losses of cations and P there have been only minor weathering-related elemental losses in bulk due to abundant unweathered >2-mm rock fragments in the soils. In this low rainfall environment soil development is influenced mainly by formation of pedogenic carbonate and some loss of surface horizon material via wind erosion. For MAP from ~700 mm to 2100 mm, unweathered >2-mm rock fragments are restricted to the deepest soils, bulk elemental losses are greater than at the lower MAP sites and P is enriched in surface soil horizons relative to abundances in deeper soils. For MAP >2100 mm, cations have been extensively leached from the soils, aluminum mobility and iron redox processes predominate and soil fertility is low. The distribution of radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) in the exchange and bulk soil pools reveals dominance of basalt-derived Sr up to the 2100-mm MAP threshold, and precipitation- and Asian dust-derived Sr in those pools at the wetter sites at higher elevation (Stewart et al., 2001).

3. Material and methods

Soils from previously well-characterized depth profiles at six sites along the climosequence (Figure 1) were selected for Ca, Sr and Ba isotope analysis: site B (185 m; 250 mm) and site E (elevation: 674 m; MAP: 720 mm), within the domain of pedogenic carbonate formation and wind erosion; site I (1090 m; 1750 mm) and site J (1134 m; 1910 mm), within the domain of enhanced primary mineral weathering and biolifting of nutrients; and site M (with associated sub-site MF)

(1200 m; 2380 mm) and site L (1254 m; 2980 mm) within the domain of Al mobility and Fe enrichment. We note that the rainfall values assigned to these sites are derived from the on-line rainfall atlas of Hawaii (Giambelluca et al, 2012). They are similar to those given in Vitousek and Chadwick (2013), but different from those given in Chadwick et al (2003) and Porder and Chadwick (2009) which relied on an older version of the rainfall atlas (Giambelluca et al, 1986). Differences in rainfall values are due to different time bases for instrumental measurements and differences in interpolation methods (see Giambelluca et al (2012) for details).

For this study we obtained concentration and isotope ratio data for Ca, Sr and Ba in the exchangeable component of the <2-mm fraction of 40 selected soil samples from these sites. In addition we augmented the composition data for HVS deposits reported by Spengler and Garcia (1986) by analyzing eight previously collected lava and tephra fragments from several soil pits for chemical and Ca, Sr and Ba isotope compositions. Lava fragments were collected from the bottom of pits at sites B and E. Tephra fragments were collected from the bottom of pits at sites I, M, P (site described in Chadwick et al., 2003) and from the 0-10 cm, 10-20 cm and 50-70 cm depth intervals at site B. We likewise analyzed a sample of pedogenic carbonate from low-MAP site B for Ca isotope composition. Finally, to provide context on the role of plants during early stages of weathering of Hawaiian lavas an Ohi'a (*Metrosideros polymorpha*) tree seedling and attached rock fragments were collected from a lava flow associated with the 1955 eruption along the East Rift Zone of Kilauea in the Puna District at the southeast corner of Hawaii. The seedling was separated into root, stem and foliage fractions which along with the rock fragments were analyzed for Ca, Sr and Ba concentrations and isotope compositions.

3.1 Sample preparation

Soil samples from five sites (B, I, M, MF, L) analyzed during the early stages of this study were subjected to a two-stage leaching procedure to compare chemical and isotope compositions of water-available and exchangeable fractions in order to test the fidelity of the soil cation exchange pool as a record of the composition of infiltrating soil water. Soils from sites E and J were analyzed during the later stages of this study and did not receive the initial water leach. To isolate the water-available fraction of soils, approximately 1g of soil (<2-mm fraction) was mixed with 25mL of distilled water and shaken continuously for 72 hours. The resulting solution was filtered (0.45- μ m pore size) and reserved, while the remaining soil was mixed with 50mL of 0.1N ammonium acetate and shaken continuously for 24 hours to isolate the exchangeable fraction. 1mL of the product exchangeable solution was filtered (0.45- μ m pore size) and diluted 1:10 with distilled water. The water extract and exchangeable dilutions were adjusted to 3% HNO₃ relative concentration using Teflon distilled HNO₃ to obtain solutions for chemical analysis. For samples having measurements of both water extract and exchangeable fractions the isotope compositions of the total exchangeable fraction were calculated as the mass-weighted sum of the operational water extract and subsequent exchangeable fractions using concentration data and isotope data for each fraction. However, as only a subset of the water extract fractions were measured for Sr and Ba isotope compositions, the exchangeable fraction for samples not having a measured water extract fraction was assumed to be identical to the measured exchangeable fraction based on the essentially 1:1 correspondence of measured water extract and exchangeable fractions (discussed below).

Ohi'a tree seedling tissues, attached rock fragments, HVS rock samples and the sample of pedogenic carbonate were totally digested using Teflon-distilled ultra-pure acids. Approximately 250 mg of Ohi'a root, stemwood and foliage tissues were digested in 10 mL concentrated HNO₃ in

closed Teflon vessels at ~50°C for 48 hours. Prior to digestion the Ohi'a roots were sonicated in several distilled water baths to remove attached rock microfragments. One mL of each product digest solution was diluted 1:33 with distilled water to obtain a 3% HNO₃ solution for chemical analysis. Approximately 100 mg of powdered HVS and Ohi'a tree site rock samples were digested using a two-stage procedure, first in a mixture of 3 mL of concentrated HF and 0.5 mL of concentrated HNO₃ in a closed Teflon vessel at ~50°C for 24 hours and second, following evaporation, in 10 mL of 6N HCl in the closed Teflon vessel at ~50°C for an additional 48 hours. The sample of pedogenic carbonate (100 mg) was digested in 10 mL of 6N HCl in a closed Teflon vessel at 50°C for 24 hours. A 2 mL cut of each digest solution was then evaporated and the solid residue re-dissolved in 50 mL of 3% HNO₃ to obtain the solution for chemical analysis.

3.2 Analytical protocols for element concentration and isotope analysis

Element concentrations were measured using a Perkin-Elmer Elan6000 quadrupole inductively coupled plasma mass spectrometer. For analysis of water and exchange extracts and plant tissue solutions, synthetic standards spanning the anticipated composition range were used to build calibration curves for Ca, Sr and Ba, giving r-squared correlations better than 0.99 for all elements. For analysis of rock digest solutions, a set of ten international rock standards digested using identical procedures was used to build calibration curves for all elements reported. Beryllium was used as the internal standard for analysis of lithium, germanium was used as the internal standard for elements having mass between sodium and niobium, and thallium was used for elements heavier than cesium to correct for drift in instrument sensitivity and matrix effects. Reported concentrations are precise to better than 5%. SiO₂ concentrations were calculated by subtracting concentrations of other metal oxides and loss on ignition (i.e. weight loss following baking of rock powder at 650°C for 24 hours in a muffle furnace) from 100%.

Calcium, Sr and Ba stable isotope ratios were determined using “double spike” thermal ionization mass spectrometry (TIMS). Each element was purified for measurement of isotope ratios using cation column exchange chromatography (Biorad AG50-X8, 200-400 μ mesh). For Ca, sufficient exchange, plant digest or rock digest solution to supply 1.5 μ g of Ca was mixed with a fixed amount of double spike solution substantially enriched in ^{42}Ca and ^{43}Ca compared to natural levels (^{42}Ca - ^{43}Ca double spike). A pure (and in particular Sr-free) fraction of Ca was obtained from the exchange column using 2*N* HCl as the eluent (column dimensions: 0.7cm diameter, 10cm resin height, 4cm³ resin volume; Ca was obtained in the 18-25 mL 2*N* HCl fraction). For Sr and Ba, sufficient exchange, plant digest or rock digest solution to supply 1 μ g of each element was mixed with a fixed amount of either ^{84}Sr - ^{87}Sr or ^{132}Ba - ^{136}Ba enriched double spike solution. An additional purification of an unspiked Sr aliquot was carried out for all samples using separate columns in order to allow measurement of the “traditional” $^{87}\text{Sr}/^{86}\text{Sr}$ ratio required to deconvolute the spiked Sr measurements. Pure Sr and Ba fractions were obtained from the ion exchange columns using 2*N* HCl as the eluent (column dimensions: 0.5cm diameter, 5cm resin height, 1cm³ resin volume; Sr was obtained in the 7-12 mL 2*N* HCl fraction, Ba was obtained in the 16-23 mL 2*N* HCl fraction). 50 μ L of 0.1*N* H₃PO₄ was added to each column product solution which was then evaporated and converted to nitrate form using concentrated HNO₃. All samples were treated with a mixture of concentrated HNO₃ and 30% H₂O₂ on low heat to the point of evaporation to eradicate organics. For Ca, Sr and Ba, samples were loaded with H₂O onto the sample portion of a double rhenium filament assembly for TIMS analysis.

Calcium isotope ratios were measured using a Finnigan MAT 261 fixed multi-collector TIMS instrument fitted with four collectors that simultaneously monitor ^{40}Ca , ^{42}Ca , ^{43}Ca and ^{44}Ca ion beams. Filament currents were typically 1.8A for the evaporation filament and 2.6A for the

ionization filament. ^{40}Ca ion beams were maintained at approximately 1.5V. Sr and Ba isotope ratios were measured using a Finnigan MAT 261 adjustable multi-collector TIMS instrument. For Sr, the ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr ion beams were monitored simultaneously. Filament currents were typically 1.8A for the evaporation filament and 2.6A for the ionization filament. ^{88}Sr ion beams were maintained at approximately 3V. For Ba, the ^{132}Ba , ^{134}Ba , ^{136}Ba , ^{137}Ba and ^{138}Ba ion beams were monitored simultaneously. Filament currents were typically 1.5A for the evaporation filament and 2.6A for the ionization filament. ^{138}Ba ion beams were maintained at approximately 6V. For all measurements, data was collected for 10 blocks of 10 8-second static measurements, with a baseline measurement between each block at half mass.

$^{87/86}\text{Sr}$ ratios measured on unspiked samples were internally normalized assuming a value of 8.37521 for $^{88/86}\text{Sr}$. For Ca, Sr and Ba stable isotope measurements, double spike subtraction was accomplished using a spreadsheet algorithm that assumes exponential mass dependent fractionation during both column purification and TIMS analysis. Results for the stable isotope measurements are expressed in standard “delta notation”, the permil difference of the measured ratio of a sample compared to average values for NIST 915A for Ca, NIST 987 for Sr, and NIST 3104a for Ba. Reported values represent the average of two total procedural replicates for each sample which agreed to better than 0.12‰ for $^{44/40}\text{Ca}$, 0.021‰ for $^{88/86}\text{Sr}$ and 0.05‰ for $^{138/134}\text{Ba}$.

On the TIMS instrument used for Sr isotope measurements the $^{87/86}\text{Sr}$ ratio for unspiked NIST 987 was 0.71024 over the period of this study. For Ca, three standards (NIST 915A, La Jolla Ca, column processed seawater) were included on each sample wheel. During the course of this study, 15 measurements of La Jolla Ca yielded $\delta^{44/40}\text{Ca} = 0.69\text{‰}$ ($2\sigma=0.07\text{‰}$) and 15 measurements of seawater yielded $\delta^{44/40}\text{Ca} = +1.93\text{‰}$ ($2\sigma=0.08\text{‰}$) relative to the average of 15 measurements of NIST 915A ($\delta^{44/40}\text{Ca} = 0\text{‰}$, $2\sigma=0.05\text{‰}$). This value for seawater is identical to that reported in the

compilation of Fantle and Tipper (2014). Six measurements of Ca purified from BHVO (Hawaiian) basalt yielded $\delta^{44/40}\text{Ca} = +0.98\text{‰}$ ($2\sigma=0.07\text{‰}$) relative to the NIST915A average. This value for BHVO is identical to that reported by Huang et al (2011). For Sr, two standards (NIST 987, column processed seawater) were included on each sample wheel. During the course of this study, 10 measurements of seawater yielded $\delta^{88/86}\text{Sr} = +0.395\text{‰}$ ($2\sigma=0.012\text{‰}$) relative to the average of 10 measurements of NIST 987 ($\delta^{88/86}\text{Sr} = 0\text{‰}$, $2\sigma=0.010\text{‰}$). This value for seawater is identical to that reported by Krabbenhoft et al (2009). Six measurements of Sr purified from BHVO basalt yielded $\delta^{88/86}\text{Sr} = +0.245\text{‰}$ ($2\sigma=0.011\text{‰}$) relative to the NIST987 average. This value for BHVO is identical to that reported by Moynier et al (2010) and somewhat lighter than but statistically identical to that reported by Charlier et al (2012) given the large standard errors for the measurements reported by these latter workers. For Ba, there are no recognized standards available for routine analysis, but suitable candidates are currently being considered including NIST 3104a. Six measurements of Ba purified from BHVO basalt yielded $\delta^{138/134}\text{Ba} = +0.06\text{‰}$ ($2\sigma=0.04\text{‰}$) relative to the average of 10 measurements of NIST 3104a as a provisional zero point for the delta scale ($\delta^{138/134}\text{Ba} = 0\text{‰}$, $2\sigma=0.03\text{‰}$).

4. Results

4.1 Chemical and isotopic compositions of HVS samples

Selected oxide and element concentrations pertinent to this study as well as Ca, Sr and Ba isotope compositions for the 8 lava and tephra fragment samples analysed for this study are given in Table 1. The SiO_2 concentrations indicate that the rocks span a range from evolved hawaiite to mugearite and thus correspond to much of the compositional range of HVS lavas reported by Spengler and Garcia (1986). Ca and Sr concentrations vary by a factor of 3 and generally decrease with increasing SiO_2 while Ba concentrations vary by a factor of 2 and generally increase with

increasing SiO₂. The large compositional range represented by these samples suggests that designation of a single soil parent composition for purposes of Ca, Sr and Ba mass gain/loss calculations would likely be problematic.

Stable isotope compositions of Ca are quite variable ($\delta^{44/40}\text{Ca}_{\text{NIST915A}} = +0.37$ to $+0.97\text{‰}$). To our knowledge, these are the first Ca stable isotope measurements of volcanic rocks from a single volcano. Previous work on Ca stable isotopes in igneous rocks focused mainly on reconnaissance surveys and only rarely on geographically restricted sample sets. For example, DePaolo (2004) reported a range of $\delta^{44/40}\text{Ca}_{\text{NIST915A}}$ spanning 0.7‰ ($+0.65$ to $+1.25\text{‰}$) for a global selection of igneous rocks. Huang et al (2011) reported a range of $\delta^{44/40}\text{Ca}_{\text{NIST915A}}$ spanning 0.27‰ ($+0.75$ to $+1.02\text{‰}$) for 12 Hawaiian shield-forming tholeiitic basalts. We note that the tephra fragment from site B (10-20cm) has the lightest Ca yet measured in an igneous rock.

Stable isotope compositions of Sr are likewise quite variable ($\delta^{88/86}\text{Sr}_{\text{NIST987}} = -0.02$ to $+0.27\text{‰}$). As with the Ca isotopes, these are to our knowledge the first Sr stable isotope measurements of volcanic rocks from a single volcano and previous work on igneous rocks has focused mainly on reconnaissance surveys. For example, Charlier et al (2012) reported a range of $\delta^{88/86}\text{Sr}_{\text{NIST987}}$ spanning 0.6‰ (-0.2 to $+0.4\text{‰}$) for a global selection of igneous rocks with samples having values less than $+0.1\text{‰}$ restricted to high-SiO₂ rocks such as silicic tuffs. We note that the tephra fragment from site B (10-20cm) has the lightest Sr yet measured in igneous rocks other than these high silica rocks. Values of $^{87/86}\text{Sr}$, obtained primarily for deconvolution of the double spiked stable Sr isotope measurements, are for the most part very restricted and similar to those obtained by Hoffmann et al (1987) for HVS lavas ($^{87/86}\text{Sr} = 0.7035$ - 0.7036). However, the three mugearitic tephra fragments from site B have $^{87/86}\text{Sr}$ values more typical of the underlying Polulu shield

forming flows ($^{87/86}\text{Sr} = 0.7036\text{--}0.7039$) hinting at assimilation of Polulu material by the evolved HVS magmas.

In contrast to the Ca and Sr stable isotopes, Ba stable isotope compositions of the HVS samples are relatively homogeneous ($\delta^{138/134}\text{Ba}_{\text{NIST3104a}} = -0.02$ to $+0.10\text{‰}$). Again to our knowledge these are the first Ba stable isotope measurements of igneous rocks to be reported in the literature and thus there are no external datasets for comparison. The lead author has measured Ba isotope compositions in a suite of international igneous rock standards ranging in composition from basalt to rhyolite/granite revealing a total range spanning 0.22‰ ($\delta^{138/134}\text{Ba}_{\text{NIST3104a}} = +0.03$ to $+0.25\text{‰}$). Thus while there may be intriguing Ba stable isotope variability in igneous rocks overall, the range observed in the HVS samples is only slightly greater than the precision of the measurements.

4.2 Chemical and isotopic compositions of Ohi'a seedling and attached rock fragments

Concentrations and isotope compositions of Ca, Sr and Ba for the roots, stem and foliage of the Ohi'a seedling and attached rock fragments sampled from a recent lava flow on Hawaii are given in Table 2. In the seedling, concentrations of Ca increase from roots to foliage while concentrations of Sr and Ba decrease from roots to foliage. Ca/Sr ratios increase from roots to foliage, and are consistently greater than the Ca/Sr ratio of the lava fragments. Sr/Ba ratios are more constant across seedling tissues, and are consistently less than the Sr/Ba ratio of the lava fragments.

The stable isotope compositions of Ca, Sr and Ba of the seedling tissues are consistently lighter than those of the lava fragments, providing clear evidence that the roots preferentially take up light isotopes of these alkaline earth elements even from fresh rock substrate in the absence of significant soil. Foliage contains the heaviest Ca, Sr and Ba, while roots contain the lightest Sr and

Ba and stemwood the lightest Ca. Values of $^{87/86}\text{Sr}$ in the seedling tissues are greater than that of the lava fragments most likely reflecting a marine influence via precipitation. A simple mass balance between rock Sr ($^{87/86}\text{Sr} = 0.70386$) and marine Sr ($^{87/86}\text{Sr} = 0.70917$) reveals that Sr in the seedling tissues ($^{87/86}\text{Sr} \sim 0.705$) is approximately 20% marine component. However as discussed below this marine contribution via atmospheric deposition is not likely to influence apparent plant-rock isotope fractionation factors.

4.3 Chemical and isotopic compositions of water extract and exchangeable soil fractions

A common assumption in soil studies is that the composition of the soil exchange pool reflects the composition of soil water in some predictable manner. For example, one element may have greater sorption potential than another leading ideally to predictable differences in the concentration ratio of those elements for dissolved and sorbed fractions. Likewise it is conceivable that isotopic contrasts between dissolved and sorbed fractions might occur due to differences in binding strengths of mineral surface sites and aqueous complexes. For this study we tested this assumption on a subset of the soils using a water extract step prior to removing exchangeable cations. The water extract removed only a small fraction of sorbed cations, and we assume that agitation of the soil-water slurry for 24 hours allowed the dissolved and remaining sorbed fractions to approach equilibrium.

Chemical and isotope data for the water extract and exchangeable fractions are reported in Table 3 and Table 4, respectively, and comparisons of these operational fractions are shown in Figure 2. The Ca/Sr ratios of the water extract and exchangeable fractions lie along or straddle the 1:1 correlation line (Figure 2a). Only data for site L that has the lowest concentrations of Ca and Sr lie significantly off (but still straddle) this line due largely to data uncertainty. This result reveals that Ca and Sr are incorporated similarly from water onto exchange sites. In contrast, the Sr/Ba

ratio of the water extract fraction is similar to or greater than that of the exchangeable fraction (Figure 2b, expanded in Figure 2c) suggesting that Ba is preferentially partitioned onto and stabilized by exchange sites relative to Sr (and Ca) although there is no apparent consistent fractionation factor. The isotope compositions of the water extract and exchangeable fractions lie along or straddle the 1:1 correlation line for the Ca, Sr and Ba systems (Figures 2d-f), suggesting that the isotope compositions measured in the exchangeable fraction are representative of those of soil water in the natural system.

5. Discussion

We first present results from background research required to properly interpret the Ca, Sr and Ba isotope compositions of the soil exchange pool and their ability to assess the role of nutrient biolifting and other pedogenic processes. These include: 1) characterization of chemical and isotopic variability of the HVS soil parent materials in order to constrain initial conditions prior to the onset of pedogenesis; 2) comparison of mass gains and losses of Ca, Sr and Ba to those of P from the soils to test for a mechanistic linkage between the alkaline earth elements and P. Using this supporting information we then focus on the Ca, Sr and Ba isotope systematics of the exchangeable fraction of the soils across the climosequence and develop a simple soil and vegetation pool box model to aid interpretation of the observed isotope distribution patterns.

5.1 Chemical and isotopic systematics of HVS soil parent materials

As reported by Spengler and Garcia (1988) HVS lavas span a broad composition range ($\text{SiO}_2 = 47.6$ to 58.5 wt. %) and display correspondingly large but systematic variations of major and trace element compositions across that range. This is an important consideration for the present study as it highlights compositional variability of the soil parent materials and thus the need to assess that variability in the soils themselves to properly interpret element mass transfers and, possibly,

isotope systematics. Spengler and Garcia (1988) attributed the systematic compositional variations across the HVS lava suite to fractional crystallization of the minerals clinopyroxene, titanomagnetite, apatite and plagioclase feldspar from parental mafic magmas. The sparsely phyrlic HVS lavas contain modal apatite and titanomagnetite but clinopyroxene phenocrysts are virtually absent and likely crystallized at moderate pressure in the crust rather than at near-surface conditions. Plagioclase is an important phase in fractional crystallization models to explain the compositional spectrum of HVS lavas, but is only rarely present as a phenocryst phase implying some form of “dynamic flow crystallization” resulting in separation of crystals from magma at depth. Amphibole occurs in the more evolved HVS lavas.

In an attempt to link HVS parent to soil compositions, we have identified the Ti/Nb ratio as a diagnostic variable that describes both magmatic differentiation (Ti loss due to magnetite fractionation, Nb as a nearly incompatible element) and soil parent lineage (both Ti and Nb are essentially immobile during rock and soil weathering, as discussed further below). Here we use the Ti/Nb ratio of HVS samples as an index to characterize chemical and isotope variations across the magmatic suite. For example Ti/Nb decreases systematically with increasing SiO₂ content as shown in Figure 3a which combines the lava compositions reported by Spengler and Garcia (1988) and our new data for lava and tephra fragments (Table 1). Later, we use the Ti/Nb ratio of each soil sample to constrain the composition of the HVS parent for that soil sample based on observed correlations for the HVS samples.

A plot of P/Nb vs. Ti/Nb (Figure 3b) for the HVS magmatic suite provides an excellent demonstration of the systematic variability across the compositional range. The parameter P/Nb varies with fractionation of apatite from parental magmas, and one interpretation of the tight correlation with Ti/Nb is that apatite co-precipitated with titanomagnetite throughout magmatic

evolution in roughly constant proportions. For the present study this relationship is of central importance as it allows us to constrain the P/Nb of the HVS parent for any soil sample (required to perform mass gain/loss calculations of the nutrient P) by relating Ti/Nb ratios of soil and parent. Similar tight correlations with Ti/Nb are observed for the ratios magnesium/Nb (Mg/Nb, with Mg controlled by fractionation of clinopyroxene) and iron/Nb (Fe/Nb, with Fe controlled by fractionation of clinopyroxene and titanomagnetite). We note that the Ti/Nb ratios of the eight lava and tephra samples analysed for this study and used to characterize isotope variability span nearly the entire range for lava samples reported by Spengler and Garcia (1988).

Inter-element relationships are somewhat more complex when considering Ca/Nb, Sr/Nb and Ba/Nb relative to Ti/Nb for the HVS samples (Figure 3c-e). The Ca/Nb ratios for lava samples reported by Spengler and Garcia (1988) form a tight correlation with Ti/Nb similar to those for P/Nb, Mg/Nb and Fe/Nb and are controlled by apatite and plagioclase fractionation. The correlation of Sr/Nb with Ti/Nb for the Spengler and Garcia (1988) data is not as tight but the overall positive relationship remains. For both the Ca/Nb and Sr/Nb relationships with Ti/Nb, the compositions of the two lava samples and two of the tephra samples analysed for this study lie within the Spengler and Garcia (1988) data for lavas. On the other hand, the compositions of the remaining tephra samples analysed for this study lie to the low Ca/Nb and Sr/Nb sides of those arrays suggesting an additional Ca removal process (e.g. enhanced late-stage plagioclase fractionation). There is no clear correlation of Ba/Nb with Ti/Nb for the Spengler and Garcia (1988) data. In detail Ba/Nb increases slightly as Ti/Nb decreases from ~350 to ~200 (i.e. reflecting incompatible behaviour of Ba), then decreases with continued Ti/Nb decrease (i.e. reflecting more compatible behaviour of Ba perhaps through incorporation in plagioclase). The

compositions of the lava and tephra samples analysed for this study lie within the Spengler and Garcia (1988) data array.

The geochemical variations of the HVS magmatic suite provide context for interpreting the Ca, Sr and Ba isotope variations observed for the eight samples analysed for this study. Variations of $\delta^{44/40}\text{Ca}$, $\delta^{88/86}\text{Sr}$ and $\delta^{138/134}\text{Ba}$ for those samples are plotted relative to Ti/Nb in Figures 4a-c. In each case delta values are greatest for the two lava samples and generally decrease with decreasing Ti/Nb for the tephra samples. Variations of $\delta^{44/40}\text{Ca}$, $\delta^{88/86}\text{Sr}$ and $\delta^{138/134}\text{Ba}$ with Nb/Ca, Nb/Sr and Nb/Ba respectively are plotted in Figures 4d-f. Using this plotting format where Nb is a nearly incompatible element, mixing of two end-members and “un-mixing” processes such as crystallization and separation of minerals from a liquid form straight line arrays. The linear trends observed for Ca, Sr and Ba are consistent with mixing of isotopically heavy and light end-member magmas to form the arrays and, for Ca and Sr, with crystallization of a Ca-Sr containing but Nb-free mineral such as plagioclase having heavy Ca ($\delta^{44/40}\text{Ca} \sim +1.1\text{‰}$) and heavy Sr ($\delta^{88/86}\text{Sr} \sim +0.31\text{‰}$) from magmas having similar composition to those of the two lava samples. The Ca and Sr isotope compositions of the plagioclase predicted by the graphical relationship are shown in Figures 4d and 4e, but stress that these values do not represent actual measurements of plagioclase from HVS materials. The crystal subtraction scenario is difficult to evaluate in the case of Ba due to the similar incompatibility of Ba and Nb in the HVS magmas (Spengler and Garcia, 1988).

The important conclusion for the present study is that observed correlations with magma chemistry and particularly the excellent correlation of P/Nb with Ti/Nb suggest that isotope variability is due to magmatic rather than weathering processes and must be considered when characterizing the isotope composition of soil parent materials. Although further interpretation of magmatic variations and eruptive sequences is beyond the scope of the present study, we note that

the apparent difference in isotope composition between lavas and tephra may be an important factor to consider when evaluating isotope distributions in soil profiles developed on volcanic materials having a complex depositional history.

5.2 Comparison of mass losses and gains of P, Ca, Sr and Ba in climosequence soils

Here we assess net gain or loss of P, Ca, Sr and Ba from soils relative to HVS parent materials at six selected sites along the climosequence to a) demonstrate the geochemical linkage of Ca, Sr and Ba with P to support use of the isotopes as proxies for nutrient biolifting, and b) reveal differences in geochemical behavior of Ca, Sr and Ba in these soils to aid interpretation of isotope systematics of the soil exchange pool. For mass gain/loss calculations we used both published and unpublished data from a pre-existing dataset which are summarized in Table 2; analytical procedures used to obtain element concentration data are given in Chadwick et al (2003). Net gain or loss of an element in soil systems is commonly assessed by considering tau values defined as:

$$\tau = ((C_{ei,w}/C_{ie,w}) / (C_{ei,p}/C_{ie,p})) - 1 \quad (1)$$

where C_{ei} is the concentration of the element of interest, C_{ie} is the concentration of an immobile element, w represents weathered horizons and p represents parent material (Chadwick et al., 1990). We used Nb as the immobile element for the calculation due to its demonstrated immobility in Hawaiian soils (Kurtz et al., 2000).

Our approach was to determine unique ratios of $C_{ei,p}/C_{ie,p}$ of the HVS parent for each soil sample by assuming identical Ti/Nb ratios in soil and parent and determining corresponding P/Nb, Ca/Nb, Sr/Nb and Ba/Nb ratios based on regressions through the HVS data (Figures 3b-e). We note that the range of Ti/Nb ratios (~100-400) observed in six soil profiles along the climosequence (Figure 5a) is virtually identical to that observed for the HVS magmatic suite. The

linkage of soils to specific HVS parent compositions relies on the assumption that Ti is immobile in these soils during weathering and pedogenesis. Kurtz et al. (2000) demonstrated that at high MAP sites along the Kohala climosequence ratios of tetravalent zirconium (Zr) and thorium (Th) to Nb (Zr/Nb and Th/Nb) were lower in shallow horizons and higher in deeper horizons compared to HVS lavas implying downward transport of Zr and Th perhaps as organic complexes. However we believe that tetravalent Ti is in fact an immobile element in this system for several reasons. First, the surface horizons at high MAP site M have Ti/Nb ratios that are similar to those of the highest-Ti/Nb HVS samples (Figure 5a) and thus cannot have lost significant Ti to downward transport. Second, although surface and deep soil horizons at the high MAP site L have similar Ti/Nb values that could reflect the homogenizing influence of downward transport of Ti, a similar pattern is observed at site E where MAP is below the threshold for downward transport of Zr and Th (Kurtz et al, 2000). Third, while Zr and Th are not important constituents of typical minerals in mafic rocks such as HVS lavas and tephra and thus reside in groundmass and glass, Ti is an essential component of resistant titanomagnetite microphenocrysts and is thus more difficult to mobilize. Thus we believe that the observed Ti/Nb ratios in Kohala soils accurately reflect HVS lavas and tephra compositions, and given the systematic variability of Ti/Nb across the HVS compositional spectrum (Figure 2a) may find additional utility such as interpretation of eruptive sequences.

The data for interpreted soil parent ratios and the corresponding τ values for P, Ca, Sr and Ba for the six soil profiles are given in Table 5. Tau values for P (τ_P) are plotted as a function of sample depth in Figure 5b. Three of the profiles (sites E, I, J; open symbols) have greater τ_P in surface soil relative to values in soil at depth while the profiles from the higher-MAP sites M and L and the low-MAP site B (closed symbols) show no enrichment of P at the surface. We note that

at site E some surface soil has likely been removed due to wind erosion and that τ_p in the removed soil could have been greater than that in the current surface soil.

Tau values for Ca (τ_{Ca}), Sr (τ_{Sr}) and Ba (τ_{Ba}), respectively, are plotted as a function of τ_p for these sites in Figures 5c-e. In each plot the 1:1 correlation line with τ_p is included to better show inter-element tau relationships. We note that the sample with the highest values of τ_{Ca} and τ_{Sr} at site B is the deepest in the profile and may reflect a component of pedogenic carbonate which has been identified at this site (Capo et al, 2000). For sites B, E, I and J these plots reveal generally positive relationships between these parameters at each site and, at given τ_p , values in the order $\tau_{Ca} < \tau_{Sr} < \tau_{Ba}$. Site-specific leaching in the order $Ca > Sr > Ba$ is clearly evident in Figure 5f which compares total soil column mass gain/loss for Ca, Sr and Ba (weighted for sample interval thickness and density) to those for P as a function of MAP. Moreover, the trends for each element in Figure 5f are consistent with increased overall leaching of Ca, Sr and Ba relative to P with increasing MAP. Although we have no rigorous explanation for the greater retention of Ba relative to Ca and Sr on exchange sites, Ba is observed to be more strongly complexed by organic matter than Ca and Sr in the oceans and its geochemical behavior parallels that of P to a large degree (e.g. Dymond et al 1992; Schoepfer et al, 2014). The trends observed in Figure 5f might represent very dynamic relative changes in the interactions of the alkaline earths and P with soil organic matter with variable MAP and soil development.

It is worthwhile to consider the potential influence of uncertainty in assigning unique parent compositions to individual soil samples given the scatter of HVS data around the correlation lines shown in Figures 3b-e. As a measure of the uncertainty of our soil parent estimation method we calculated the standard error (SE) associated with each data regression shown in Figures 3a-d: P/Nb, SE=10; Ca/Nb, SE=115; Sr/Nb, SE=6; Ba/Nb, SE=1.4. By visual inspection we found that

the parameter $2*SE$ provides a reasonable estimate of the maximum range of (P,Ca,Sr,Ba)/Nb ratios at given Ti/Nb across the range of HVS samples. The ranges of tau values calculated for $\pm 1SE$ around reported values lie within the plotted symbol for all but two samples in Figures 5b-e, and in all cases the general graphical relationships are essentially unchanged by considering that uncertainty and the observations given above remain robust. Thus we feel that our calculation method provides a reasonable approximation of soil parent compositions and is clearly a better approach than assuming a single average parent composition given the broad yet systematic compositional range of HVS lavas and tephra.

5.3 Ca, Sr, Ba isotope systematics of soil exchangeable fractions

Isotope data for the exchangeable fraction of soils at sites E, I and J, which all have greater τ_p in the shallowest horizon relative to values in soil at depth, and from the highest MAP site L for comparison are plotted in Figures 6a-c. In addition, several pertinent system components that have bearing on interpretation of isotope variations of the exchange pool are included in these plots. The shaded band in each figure shows the range of isotope composition of the HVS lavas and tephra measured in the samples for this study, helping to characterize the isotope composition of soil parent materials. In addition, values are shown for the isotope composition of Ca (Zhu and Macdougall, 1998), Sr (Fietzke and Eisenhauer, 2006) and Ba (Horner et al, 2015) in seawater that may influence the composition of aerosols in this near-marine setting. We note that although the Ba isotope composition of seawater has only recently been provisionally characterized ($\delta^{138/134}Ba=+0.3\text{‰}$ for deep water, $+0.6\text{‰}$ for surface water from the south Atlantic Ocean; Horner et al, 2015), greater $\delta^{138/134}Ba$ relative to lithologic inputs to the marine cycle is consistent with precipitation of isotopically light barite in the water column as an important control on marine Ba concentrations (Gonneea and Paytan, 2006; Von Allmen et al., 2010). Finally, the horizontal

labelled line along the isotope axis in each plot shows the isotope compositions of Ohi'a tree tissues (R=roots, S=stem, F=foliage; Table 2) for the seedling plucked from a recent Hawaiian lava flow. Based on our analysis of rock fragments attached to the roots (Table 2), this lava flow has Ca, Sr and Ba isotope compositions that are nearly identical to the heaviest HVS samples.

At sites E, I and J the shallowest soil horizons have the lightest isotope compositions of exchangeable Ca, Sr and Ba, all of which lie to the light side of the vertical band defining the range of HVS soil parent materials. Exchangeable Ca and Sr in the shallowest samples have among the lightest isotope compositions yet reported for terrestrial samples, similar to those of plant tissues measured in other studies (e.g. Page et al, 2008; de Souza et al., 2010) and lighter than those of marine carbonates ($\delta^{44/40}\text{Ca} = +0.7 \pm 0.7\text{‰}$, Fantle and Tipper, 2014; $\delta^{88/86}\text{Sr} = +0.28 \pm 0.13\text{‰}$, Halicz et al, 2008) which comprise the lightest global lithologic pool for Ca and Sr yet considered. For the Ca, Sr and Ba systems, these light isotope compositions project toward the range for the Ohi'a seedling tissues which we assume are representative of plants growing on fresh lavas similar to HVS parent materials having the heaviest isotope compositions. Plants which grew on fresh, highly evolved and possibly isotopically light HVS flows and tephra may have had even lighter isotope compositions. Taken together these data suggest that during initial weathering and subsequent pedogenesis at these sites, plants have selectively taken up light Ca, Sr and Ba from the HVS parent materials and provided a light biocycled component available for concentration in the near-surface exchangeable fraction. We note that at site E wind erosion may have removed an even lighter biocycled pool than is evident in present-day surface soils.

With increasing depth at sites E, I and J exchangeable Ca, Sr and Ba all become heavier although the patterns of increasing heaviness differ between the systems. The patterns for Ba isotopes are particularly striking in that exchangeable Ba for all samples below the shallowest

sample at each site is heavier than Ba in possible HVS parent materials. We note that the Ba isotope compositions of many of the deeper exchange fractions approach that of our provisional seawater value but view this as fortuitous since 1) evidence from $^{87/86}\text{Sr}$ reveals that Sr on exchange sites at sites E, I and J is primarily HVS rock-derived (Stewart et al., 2001); and 2) the Sr/Ba ratio of seawater (~1000; Bernat et al., 1972) is orders of magnitude greater than that of HVS rocks (~0.5-3; Table 1) and thus the impact of adding a seawater component to exchange sites should be much greater for Sr than for Ba.

The increase in heaviness with depth for the Ca and Sr isotope patterns at sites E, I and J is more gradual than for Ba, which as suggested by the tau data above likely reflects greater “leakiness” of Ca and Sr from the shallow soil horizons during infiltration of precipitation. In a leaky situation, light plant-associated (“biocycled”) Ca and Sr leached from shallow soil horizons would continually overprint the deeper exchange sites while light biocycled Ba is more efficiently retained by the shallow soils resulting in the characteristic isotope profiles. $\delta^{44/40}\text{Ca}$ values of the deepest samples at these sites match those of the heaviest HVS samples while $\delta^{88/86}\text{Sr}$ values of those samples lie in the middle of the range for HVS samples.

The impact of progressive leaching of Ca and Sr from, but retention of Ba by shallow soils is evident in the isotope profiles for exchangeable fractions at the high MAP site L shown for comparison in Figures 6a-c. At this site the isotope compositions of exchangeable Ca and Sr are shifted toward seawater values and the isotopic imprint of light biocycled Ca and Sr in shallow soils has been lost. The similar down-profile variations of $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ may in part reflect the influence of dust at different depths. For example relatively light Ca and Sr in the 10-30cm depth range correspond to the greatest dust-derived quartz contents in this profile (Chadwick et al. 2003). In contrast, the Ba isotope compositions at site L are shifted toward the plant values

616 compared to those at the lower MAP sites and for the deepest samples overlap those of HVS
617 parent materials. The shallowest samples at site L have retained a record of light biocycled Ba in
618 spite of near total leaching of most cations from these wet soils (Chadwick et al., 2003).

619 Two additional site comparisons allow us to examine how the isotope composition of the soil
620 exchange pool can be modified by processes such as secondary mineral formation and site
621 disturbance/land use change. First we compare isotope profiles for the exchangeable soil fractions
622 at the two driest sites B and E (Figures 7a,b,c) which should be generally similar since soils at
623 these sites have evolved under the same soil process domain. As noted above, the Ca, Sr and Ba
624 isotope profiles at site E are consistent with surface accumulation and variable leakage of
625 biocycled alkaline earth metal. At site B, the Ba isotope profile is virtually identical to that at site E
626 indicating that surface accumulation of biocycled Ba has occurred at this site. On the other hand, at
627 site B $\delta^{44/40}\text{Ca}$ values for all but the deepest sample and the $\delta^{88/86}\text{Sr}$ value for the shallowest sample
628 lie within the corresponding ranges for HVS parent materials. Thus there is no clear isotopic
629 evidence for retention of biocycled Ca or Sr at site B even though the deepest sample has heavier
630 Ca and Sr than HVS parent materials suggesting loss of a light fraction.

631 Pedogenic carbonate is a common secondary mineral at site B and the Ca isotope composition
632 of the carbonate sample analyzed for this study ($\delta^{44/40}\text{Ca}_{\text{NIST915A}} = -0.25\text{‰}$) lies to the light side of
633 values for site E (Figure 7a). Given that the three intermediate depth samples at site B have
634 extremely low Ca/Sr ratios for the exchangeable fraction (Table 3), we suggest that $\delta^{44/40}\text{Ca}$ of soil
635 water and thus the exchangeable fractions of these three soils have been shifted from values more
636 similar to those of intermediate depth samples at site E to heavier values due to formation of high-
637 Ca/Sr pedogenic carbonate. Thus the shape of the Ca isotope profile at site B may have been more
638 similar to that for Sr (i.e. heavier shallowest and deepest samples, lighter intermediate-depth

samples) in the absence of pedogenic carbonate formation, but again neither profile would suggest surface accumulation of biocycled Ca and Sr.

However, the “bowed” shape of the Ca and Sr isotope profiles may be due in part to changes in parent material compositions (i.e. tephra giving way to lava) with increasing depth. As shown in Figure 5a the three deepest samples at site B have the least Ti/Nb values measured and based on parent material isotope variations shown in Figure 4 could have had relatively light initial Ca and Sr isotope compositions. In contrast the two shallowest samples at site B have significantly greater Ti/Nb and thus could have had relatively heavy initial Ca and Sr isotope compositions that likewise could have been heavier than those of the exchangeable fractions, consistent with surface accumulation of biocycled Ca and Sr. We reiterate that wind erosion at both sites B and E may have removed an even lighter Ca, Sr and Ba biocycled fraction than is currently observed at the surface. Although speculative, this proposed scenario seems realistic given the strong evidence for surface accumulation of biocycled Ba at site B.

In the second comparison, isotope profiles at adjacent sites M and MF reveal a gradient of responses of Ca, Sr and Ba to land disturbance (Figures 7d,e,f). Site M was forested until the early 1900’s but is now an open field with dominant grass cover, while site MF is just beyond the perimeter of that field and still forested. The sites are ~100m apart and their isotope profiles were likely similar prior to the deforestation and land use change (i.e cattle grazing) at site M. We note that concentrations of exchangeable Ca, Sr and Ba are greater at site M compared to those at site MF (Table 3) reflecting mobilization of these metals from some soil pool (e.g. metal complexation with soil organic matter) not sampled by our operational exchange procedure for site MF samples. Isotope compositions of exchangeable Ca, Sr and Ba in the shallowest soils at both sites are lighter than those of HVS parent materials consistent with a biocycling legacy. At site MF the Ca, Sr and

Ba isotope profiles are intermediate between those for lower MAP site J and higher MAP site L (compare to Figures 6a,b,c). Furthermore at site MF $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ values of exchangeable Ca increase immediately below the surface sample to constant values approaching those observed at the highest MAP site L (compare to Figures 6a,b). At site M, however, $\delta^{44/40}\text{Ca}$ is constant down to 100cm depth then increases to values similar to those of the heaviest HVS parent materials while $\delta^{88/86}\text{Sr}$ increases continuously over the profile to values similar to those of the heaviest HVS parent materials. The shapes of the Ca and Sr isotope profiles for site M are consistent with net downward transfer of light biocycled Ca and Sr from the surface to exchange sites of deeper soils in response to removal of forest cover and loss of biocycling power. In contrast, the isotope profiles for $\delta^{138/134}\text{Ba}$ at sites M and MF are similar, suggesting that disturbance at site M did not cause a significant modification of the Ba isotope distribution in these soils.

5.4 Assembling the evidence for nutrient biolifting

A major goal of this study was to assess the importance of processes influencing pedogenesis (e.g. chemical weathering, secondary mineral formation, atmospheric deposition, hydrologic transport) and particularly the importance of nutrient biolifting along the Kohala climosequence by establishing a mechanistic linkage between Ca, Sr and Ba and the nutrient P and interpreting Ca, Sr and Ba stable isotope compositions of the soil exchange pool. An important conclusion of this study is that mass gain/loss (τ) patterns for Ca, Sr and especially Ba generally track those of P in these soils. We found that there are broad site-specific positive relationships for all sites except the high MAP sites M for Ca and Sr and L for Ca, Sr and Ba (Figures 5c-e). Tau values are consistently in the order Ba>Sr>Ca at any site and decrease for all these elements relative to P with increasing MAP (Figure 5f), which points to a spectrum of leakiness of these alkaline earth metals in the order Ca>Sr>Ba from these soils. Another important conclusion is that plants growing on a

685 fresh lava surface in the absence of a significant soil exchange pool preferentially take up light Ca,
686 Sr and Ba isotopes from the rock providing an isotopic fingerprint of biolifting. This latter result
687 supports the concept that plants form an ecosystem pool having sufficiently light Ca, Sr and Ba to
688 leverage isotope compositions of the exchangeable fraction of soils.

689 Recent work has demonstrated that isotope compositions of the soil exchange pool are
690 established and evolve primarily in response to changes in elemental fluxes to and from that pool,
691 particularly as a result of isotope fractionation during plant nutrient uptake and recycling. These
692 efforts have focused on Ca isotope systematics due simply to the abundance of isotope data on
693 rocks (silicates, carbonates), rain and dust, plants and water; see Fantle and Tipper (2014) for a
694 thorough review of data and modeling approaches. For example in their study focused on
695 constraining the isotope mass balance for a forested ecosystem, Holmden and Belanger (2010)
696 developed a three-box model of the cycle of plant available Ca in a boreal forest by considering
697 the interactions between the forest floor and mineral soil “boxes” and trees. Their model evaluated
698 the impact of atmospheric deposition, soil mineral weathering and plant uptake and cycling on the
699 isotope balance of Ca in the soil exchange pool. They viewed the soil exchange pool as
700 representative of “plant available Ca”, and modeled the effect of changing relative fluxes of Ca
701 between mineral soil, forest floor and tree components.

702 Holmden and Belanger (2010) concluded that the most important leverage on the isotope
703 composition of forest floor exchangeable Ca is the relative roles of nutrient uptake through roots in
704 the forest floor vs. roots in the mineral soil and recycling through decomposition of litterfall.
705 Calcium derived from abiotic mineral weathering and atmospheric deposition at their study site
706 were found to be isotopically similar and provided little leverage on the isotope composition of the
707 exchange pool. Using real data from their study site Holmden and Belanger (2010) showed that

$\delta^{44/40}\text{Ca}$ of the forest floor exchange pool can be driven to positive values relative to bedrock by increasing the uptake flux from the forest floor relative to the litterfall/recycling flux back into the forest floor. Fantle and Tipper (2014) obtained similar results using a modeling approach constrained by data from the Strengbach catchment in France, then expanded the analysis to consider the implications of the different timing of uptake and recycling terms on an annual basis.

Increased uptake flux from the forest floor exchange pool relative to the recycling flux to that pool would be the case for an aggrading forest when uptake from the forest floor exchange pool is more important than uptake from deeper soil pools, or when total uptake and litterfall fluxes are balanced but some of the litterfall flux is lost to either leakage or some soil pool (e.g. oxalate) other than the forest floor exchange pool. Alternatively the models developed by Holmden and Belanger (2010) and Fantle and Tipper (2014) can be used to show that $\delta^{44/40}\text{Ca}$ of the forest floor exchange pool can be driven to negative values relative to bedrock by increasing the litterfall/recycling flux to the forest floor relative to the uptake flux from the forest floor. This would be the case for a degrading forest, with the light Ca from decomposing vegetation being added mainly to the forest floor exchange pool, or when total uptake and recycling fluxes are balanced but biolifting from the mineral soil is important such that less uptake from the forest floor exchange pool is required to maintain balance.

5.4.1 A model of exchange pool isotope variability

In order to relate these findings to the present study and to illustrate the isotopic shift described above, we constructed a simple finite difference flux-based model for Ca in the Kohala soils following the approach presented in Holmden and Belanger (2010). The model seeks to explain observed isotope variations in a shallow soil horizon exchange pool box (0-10cm depth), a deep soil exchange pool box (below 10cm depth) and a vegetation pool (Figure 8a), and is applicable to

the Sr and Ba systems as well. As developed here the model focuses on plant uptake flux from and recycling flux to the soil exchange pools within the context of plant-soil and within plant isotope fractionation factors. In addition the model considers the potential influence of additional fluxes within the total ecosystem box structure such as leakage of soil solution from surface to deep exchange sites (f_z), mineral weathering (f_w), groundwater recharge (f_{gw}) and atmospheric sources (f_a). We note that the fluxes f_z , f_w and f_{gw} influence the size and isotope composition of soil exchange pools but do little to change the relative isotope distributions derived from varying the uptake and recycling flux terms. In the model scenarios given below, f_w , f_z and f_{gw} are used mainly to adjust Ca concentrations in the soil and vegetation pools.

Before presenting our model scenarios the influence of atmospheric deposition (f_a) on isotope distributions in the soil exchange pool deserves special attention. Of particular importance is the potential role of seawater in determining isotope compositions of precipitation in the near coastal setting of the Kohala climosequence. We did not measure precipitation for this study, mainly because we worked with archived soil and rock samples and the field infrastructure was not in place to rigorously sample precipitation events. However, although it seems logical to suggest that seawater might have an influence on isotope compositions of precipitation in this setting and that increasing the precipitation input could help to shift exchange pool isotope compositions to heavier values, evidence from measurement of precipitation elsewhere suggests that the seawater signature is commonly masked by other components of precipitation such as carbonates and mineral dust. For example, Fantle and Tipper (2014) evaluated all current data on the Ca isotope composition of rain finding a mean value for $\delta^{44/40}\text{Ca}_{\text{NIST 915}} = +0.72\text{‰}$ with values ranging from 0 to +1.9‰, the latter being the accepted value for seawater. White et al. (2012) reported $\delta^{44/40}\text{Ca}$ values ranging from +0.1 to +1.3‰ for six samples of precipitation from their study site at Santa Cruz (CA)

754 directly on the Pacific coast. Additional unpublished values of $\delta^{44/40}\text{Ca}_{\text{NIST 915}}$ determined by the
755 first author for seventeen samples of precipitation from the Santa Cruz site having $^{87/86}\text{Sr}$ from
756 0.7091 to 0.7093 (i.e. essentially identical to that of seawater) averaged +0.73‰ and ranged from -
757 0.22 to +1.85‰ similar to the distribution reported by Fantle and Tipper (2014). Clearly carbonate
758 and dust components in precipitation strongly leverage at least the Ca isotope composition and in
759 many cases render it indistinguishable from that of lithologic sources (Fantle and Tipper, 2014).
760 Moreover, Ca isotope values greater than that of seawater were reported by Wiegand et al. (2005)
761 for exchangeable soil pools elsewhere in the Hawaiian Islands, revealing that processes other than
762 seawater addition influence the heaviness of at least the Ca isotope compositions of exchangeable
763 soil fractions.

764 In an initial effort to characterize Sr stable isotope systematics in precipitation, Pearce et al
765 (2015) reported measurements of $\delta^{88/86}\text{Sr}$ and $^{87/86}\text{Sr}$ in rainwater samples from Paris. Values of
766 $\delta^{88/86}\text{Sr}_{\text{NIST 987}}$ ranged from +0.13 to +0.32‰ and were interpreted to reflect mixtures of Sr derived
767 from seawater, carbonate dust and agricultural fertilizer. This range of values overlaps the heavier
768 portion of the range for HVS rock samples (Fig. 6b) and extends somewhat toward the value for
769 seawater. However, we know of no measurements of $\delta^{88/86}\text{Sr}$ in a true coastal setting and thus can
770 only suggest that Sr in precipitation along the Kohala climosequence reflects a mixture of Sr
771 derived from seawater, carbonate and silicate dust and on average is likely to be isotopically
772 indistinguishable from the HVS soil parent materials. Measurements of $\delta^{138/134}\text{Ba}$ in precipitation
773 have yet to be reported, although $\delta^{138/134}\text{Ba}$ values are likely to be dominated by dust compositions
774 due to low concentrations of Ba in both carbonates and surface seawater.

775 It is likewise important to consider the potential influence of dust on isotope distributions in
776 the soil exchange pool in this mid-oceanic setting. Dust accretion along the Kohala climosequence

is recognized mainly as a measurable proportion of quartz and mica of Asian continental origin that generally increases with increasing MAP due to dust scavenging by precipitation but is likewise recognized even at the driest sites (Chadwick et al. 2003). Although weathering of dust-derived minerals almost certainly contributes some Ca, Sr and Ba to soil waters and exchangeable fractions, several lines of evidence suggest that the influence on the isotopes is minor. Kurtz et al (2001), working with a chronosequence of soils receiving 2500 mm MAP from across the Hawaiian Islands and including a site near the Kohala climosequence, showed that the mass of accreted dust increases with increasing soil age through the 150 ky Kohala site suggesting that weathering of dust-derived minerals is suppressed relative to weathering of Hawaiian volcanic-sourced materials to this point. Stewart et al (2001) found that Asian dust-derived Sr accounted for less than 5% of the silicate fraction of soils at sites B, E, I and J which we have focused on to demonstrate nutrient biolifting with the isotope approach. Although the proportions of Asian dust-derived Ca and Ba in these soils have yet to be determined, their isotope compositions are likely to conform to the ranges for terrestrial rocks previously measured: for silicate Ca, mean = +0.94‰, $2\sigma_m = 0.04\text{‰}$, N=153 (Fantle and Tipper, 2014); for silicate Ba, range = +0.03 to +0.25‰, mean = +0.11‰, $2\sigma_m = 0.04\text{‰}$, N=11 (unpublished analyses by first author for igneous rock silicate reference materials). These values are similar to those of the HVS samples and thus provide little additional leverage on the isotope compositions observed for the exchangeable fractions.

5.4.2 Initial conditions and model scenarios

The initial conditions for the model reflect the influence of plants growing on a fresh lava surface at some point in the past. The plants obtain light Ca from the lava as an uptake flux (f_u) having isotope composition constrained by the isotope fractionation factor Δ_{uptake} . For Ca Δ_{uptake} can be estimated using data given in Table 2 for the sampled Ohi'a seedling tissues ($\delta^{44/40}\text{Ca} =$

2.01‰ to -0.60‰) and attached rock fragments ($\delta^{44/40}\text{Ca} = +0.96\text{‰}$). We have assigned a nominal average value of $\delta^{44/40}\text{Ca} = -1.0\text{‰}$ for the bulk Ohi'a seedling resulting in a value of $\Delta_{\text{uptake}} = -2\text{‰}$, but stress that this is for modeling purposes only as there is nothing unique about this assumed whole-plant Ca isotope composition. As the plants grow and Ca utilization proceeds, plant material is recycled to the surface as a litterfall/recycling flux (f_{lf}) which determines the isotope composition of an incipient surface horizon exchange pool as constrained by the isotope fractionation factor $\Delta_{\text{litter-plant}}$. Initially most of the litterfall will be foliage having Ca that is approximately 0.4‰ heavier than bulk plant Ca. As the plant community reaches a stable growth condition ($f_{\text{u}}=f_{\text{lf}}$), $\Delta_{\text{litter-plant}}$ should tend toward zero as more stemwood and decaying root material are recycled.

To this point in the model we assume that Ca has been taken up from an incipient deep exchange pool presumably developed along the surfaces of cracks in the fresh lava invaded by plant roots. The isotope composition of Ca remaining in this deep exchange pool must be isotopically heavier than the lava due to the complementary light isotope composition of the plants. To assign initial conditions to our model we have assumed that 100 units of Ca have been taken up by plants, 10 units of Ca have been incorporated in litterfall, and that for every unit of Ca taken up by plant roots 10 units of Ca remain in the developing deep exchange pool (i.e., 1000 units of Ca reside in the deep exchange pool). Thus for modeling purposes if the fresh rock is assigned a value for $\delta^{44/40}\text{Ca} = 0\text{‰}$ then initially plants have $\delta^{44/40}\text{Ca} = -2\text{‰}$, the shallow soil exchange pool has $\delta^{44/40}\text{Ca} = -1.6\text{‰}$ and the deep soil exchange pool has $\delta^{44/40}\text{Ca} = +0.22\text{‰}$ ("Init" in Figure 8b).

From this point we consider three scenarios that demonstrate the importance of relative uptake and recycling fluxes on soil box isotope compositions (Figure 8b). The starting conditions for the

first scenario are the initial conditions described above, while the starting conditions for the second and third scenarios are the final conditions of the first and second scenarios respectively. In this manner the scenarios follow the development of soil exchange and vegetation pools in a hypothetical forest/shrubland. The model proceeds by incrementally adjusting the Ca concentration and isotope composition of shallow soil, deep soil and vegetation pools through 1000 steps using the flux terms and governing equations shown in Table 6 incorporated in Figure 8.

The first scenario (“I” in Figure 8b) models biolifting in which plants take up Ca from the deep soil exchange pool only, and all Ca taken up is returned as litterfall and retained in a growing surface horizon exchange pool. In this scenario M_{ds} and M_{veg} are held constant while M_{ss} increases. A weathering flux is included to replenish Ca in the deep soil exchange pool as it is lost to plant uptake. In this case $f_{u,shallow}$ is less than f_{lf} . Over the 1000 model steps, $\delta^{44/40}\text{Ca}$ of the shallow soil exchange pool increases slightly but remains negative while $\delta^{44/40}\text{Ca}$ of the deep soil exchange pool increases to positive values. $\delta^{44/40}\text{Ca}$ of the vegetation pool tracks that of the deep soil exchange pool Ca source and eventually becomes slightly greater than that of the shallow soil exchange pool. Note that in this scenario f_a , f_z , and f_{gw} are all set to zero.

The second scenario (“II” in Figure 8b) models the situation in which plants take up Ca from the shallow soil exchange pool only and only one-tenth of that Ca is returned to the exchange pool as litterfall. In this case $f_{u,shallow}$ is much greater than f_{lf} and thus the model would apply to either an aggrading forest or delivery of a portion of the recycling flux to either leakage or some shallow soil Ca pool other than the exchange pool (e.g. a Ca oxalate pool). In this scenario M_{ds} and M_{ss} are held constant while M_{veg} increases. An atmospheric deposition flux is included to replace Ca taken up from the shallow soil exchange pool and lost to leakage to deeper soils and a weathering flux is

added to offset Ca lost to groundwater. These additional terms are added to account for the higher MAP condition implied by the need to provide Ca from atmospheric sources to replenish the shallow soil exchange pool. As the model progresses $\delta^{44/40}\text{Ca}$ of the shallow soil exchange pool shifts to positive values while $\delta^{44/40}\text{Ca}$ of the deep soil exchange pool decreases and eventually becomes more negative than that of the shallow soil exchange pool. As Ca concentration in the vegetation pool increases its Ca isotope composition becomes markedly lighter and does not track that of the shallow soil exchange pool Ca source.

The third scenario (“III” in Figure 8b) models the situation in which plants take up Ca equally from the shallow and deep soil exchange pools and 10 times the amount taken up is returned as litterfall. In this case $f_{u,\text{shallow}}$ is much less than f_{lf} and thus the model would apply to a degrading forest/shrubland. In this scenario M_{ds} and M_{ss} are held constant while M_{veg} decreases. An atmospheric deposition flux is included to replace Ca taken up from the shallow and deep soil exchange pools and lost to leakage and groundwater; no mineral weathering flux term is included. As the model progresses $\delta^{44/40}\text{Ca}$ of the shallow soil exchange pool shifts to negative values. Similarly $\delta^{44/40}\text{Ca}$ of the deep soil exchange pool decreases as the model progresses, generally tracks that of the shallow soil exchange pool and eventually becomes negative. Calcium concentration in the vegetation pool decreases considerably and its Ca isotope composition becomes more negative as the model progresses. The overall negative $\delta^{44/40}\text{Ca}$ composition of the soil-vegetation system reflects loss of heavy Ca to groundwater in scenarios II and III. While this scenario includes a significant f_a term, we note that decreasing f_a to zero and adjusting f_z and f_{gw} accordingly to hold M_{ds} and M_{ss} constant does not change the isotope distribution patterns shown in Figure 8b.

5.4.3 Isotope distributions in Kohala soils in light of the models

Given the framework provided by these model scenarios, and assuming that the pasture/forest communities along the Kohala climosequence are stable in the sense that there is no net aggradation or degradation, the fact that the Ca, Sr and Ba isotope compositions of the exchangeable fractions of the shallowest soils at sites E, I, J, and M/MF are lighter than HVS parent materials is consistent with biolifting of these elements from a deep soil pool as an important pedogenic role across much of this climosequence (scenario I). Moreover we find that the Ba isotopes provide the most consistent isotopic evidence for biolifting largely because Ba is far less susceptible to leaching than Ca and Sr. While $\delta^{138/134}\text{Ba}$ values of the exchangeable fraction of the surface soil horizons at all sites are less than those of HVS soil parent materials (Figures 6c, 7c,f), those values for deeper horizons are similar to or greater than those of the heaviest HVS soil parent materials suggesting a connection to scenario I modeled above.

A straightforward interpretation of the isotope patterns for exchangeable Ba is that Ba having the isotope composition of the HVS parent materials was mobilized during weathering and separated into two fractions, a light fraction biolifted by plants and a heavy fraction that remained in soil water and on exchange sites. Even at the high-MAP site L a light biolifted Ba fraction persists in the shallow soil exchange pool. However at site L the increase of $\delta^{138/134}\text{Ba}$ of exchangeable Ba is more gradual than at drier sites and more similar to patterns observed for Ca and Sr isotopes at the drier sites. We suggest that at site L downward leakage of light biolifted Ba and/or Ba derived from weathering of the dust fraction has overprinted the deeper exchange sites resulting in lighter Ba isotope compositions similar to those of the heaviest HVS soil parent materials.

5.5 Isotopic trends in the context of soil process domains and pedogenic thresholds

The soil process domains and pedogenic thresholds established along the Kohala climosequence (Vitousek and Chadwick, 2013) in large part represent the response of geology to hydrology including biologic influences on the hydrologic cycle. At MAP less than ~750mm/yr (sites B and E) evapotranspiration exceeds precipitation, rainfall events are sparse and episodic, soils are rarely if ever saturated and the cyclic formation of pedogenic carbonate from infiltrating precipitation at depth suggests that leakage of soil water to groundwater is minimal (Chadwick et al, 2003). There is isotopic evidence for biolifting especially in the Ba isotope proxy at both sites B and E (Figure 7c). However low values of τ_P in shallow soils at site B (Figure 5b) suggest that biolifted P has been lost from the system, probably by wind erosion and not to throughflow. A picture emerges of plants that have concentrated biolifted P in their tissues and contain isotopically light Ca, Sr and Ba being eroded and carried offshore by wind.

At MAP between 750-2100 mm/yr (sites I and J, near the upper end of this range), ecosystems are generally stable (i.e. neither aggrading or degrading), evapotranspiration and precipitation indicate a slightly positive water balance, present-day mineral weathering rates are greater than elsewhere along the climosequence and there is strong mass loss at depth and near-surface gain of P (Chadwick et al., 2007; Porder and Chadwick, 2009; Vitousek and Chadwick, 2013). At both sites I and J there is evidence for biolifting in the Ca, Sr and Ba isotope systems as well, although the evidence is strongest for the Ba isotope proxy (Figure 6c). For example at site I, the shallowest soil sample has τ_P and $\tau_{Ba} > 1$ and the lightest Ca, Sr and Ba isotope compositions for exchangeable fractions measured in this study which together support an important role for nutrient biolifting. In contrast to the lower MAP sites, leakage to groundwater becomes more important upslope due to the more positive water balance.

At MAP greater than ~2100 mm/yr (sites MF, and L), forest ecosystems are still stable but precipitation exceeds evapotranspiration, soils are moist all of the time and persistent leaching by infiltrating water has increasingly delivered most soil cations other than potassium (moderate retention in the shallowest soils) and Al, Fe and P (strong retention in mid-level to deeper soils) to groundwater (Chadwick et al., 2003). At site L a broad zone of P retention evident in the τ_p profile (Figure 5b) corresponds to a similarly distributed zone of Fe and Al retention. Within this context, the shift of Ca and Sr isotope compositions of the exchangeable fraction of shallow soils at site L to values greater than the heaviest HVS parent materials (Figures 6a,b) requires that the plant uptake flux is greater than the litterfall/recycling flux of Ca and Sr for those soils. In contrast, the Ba isotope profile at site L retains the biolifting signature, implying a greater litterfall/recycling flux than plant uptake flux from shallow soils even though downward leakage of light biocycled Ba (and/or minor dust weathering-derived Ba) is finally sufficient to overprint the isotope compositions of the deeper soil exchange sites. Decreased litterfall/recycling flux to the shallow soil exchange pool may imply that recycled Ca and Sr are simply less effectively retained by the shallow soil exchange pool than Ba and are more readily lost to leakage (f_z) and groundwater (f_{gw}). Alternatively an increasing amount of isotopically light Ca and Sr in recycled litterfall may be incorporated in some other more resilient soil pool (e.g. Ca,Sr-oxalate) and not returned to the exchange pool, which similarly would drive the remaining exchange pool to heavier isotope compositions. While occurrence and distribution of Ca oxalate has not yet been assessed in these soils, it is a common biomineral observed in plants (e.g. Franceschi and Nakata, 2005) and associated with fungi in soils (e.g. Arnott, 1995) and is likely to play some role in Kohala climosequence ecosystems.

5.6 The Ba isotope signal of biolifting across the climosequence

In terms of the exchangeable fraction the Ba isotope composition of the shallowest soil horizon at each site is lighter than the HVS parent materials while all deeper soil horizons (except at the wettest site L) have Ba isotope compositions that are heavier than those of the HVS parent materials, a consistent pattern which we attribute to inorganic nutrient (+ proxy) biolifting. Furthermore except under the most intense leaching environment at site L there is no evidence for downward leakage of light biocycled Ba overprinting the exchange fractions of the deeper soil horizons as is the case for the Sr and especially the Ca isotope profiles. The preservation of this characteristic Ba isotope profile is particularly striking given the overall loss of Ba at each site implied by τ_{Ba} values less than zero (Figure 5e). Thus loss of Ba via wind erosion of biomass and shallow soils at the lower MAP sites and via drainage of soil water to groundwater at the higher MAP sites has apparently not obscured the Ba isotope signature of biolifting.

Overall the isotope composition of exchangeable Ba in the shallowest soil horizons (top 10 cm) is fairly uniform across the climosequence, while the depth-integrated isotope composition of exchangeable Ba in deeper horizons (below 10 cm) is greatest at the low MAP sites and decreases with increasing MAP to $\delta^{138/134}\text{Ba}$ values of the HVS parent materials (Figure 9). We note that in detail although $\delta^{138/134}\text{Ba}$ of the exchangeable fraction of deeper horizons at site B is less than that at site E (i.e. in contrast to the overall pattern), exchangeable Ba in the three deepest samples at site B may be comparatively light given their overall lower Ti/Nb values relative to those of deeper samples at site E (Figure 5a) and apparent variability of $\delta^{138/134}\text{Ba}$ with Ti/Nb (Figure 4c). Moreover $\delta^{138/134}\text{Ba}$ of the exchangeable fraction of the shallow sample from site B may be elevated with respect to the shallow samples from other sites due to loss of a light fraction to wind erosion. However regardless of subtle detail the overall distribution of Ba isotopes with increasing MAP is remarkably systematic. Given the roles of relative uptake and recycling fluxes in

determining isotope compositions of the exchange pool outlined above, we interpret the decrease in $\delta^{138/134}\text{Ba}$ of the exchangeable fraction of deeper soils with increasing MAP to result from decreased uptake of inorganic nutrients from deeper sources with increasing MAP at least as reflected in the present-day Ba isotope profiles. Such a scenario implicates greater reliance on shallow sources of inorganic nutrients with increasing MAP coupled with strong retention of recycled nutrients in shallow soils to maintain light Ba isotope compositions in their exchangeable fractions.

Finally, the Ba isotope data for the exchangeable fractions straddle the field for HVS parent materials (Figure 9) suggesting that bulk soil Ba isotope compositions are unlikely to have shifted significantly from soil parent values. In fact, in the absence of fortuitous balance between shallow soil uptake and litter recycling flux terms at each site, near constant bulk isotope compositions of deeper soils at parent values are required in order to maintain near constant shallow soil exchange pool isotope compositions across the climosequence. This observation highlights the fundamental importance of the Δ_{uptake} term in determining shallow soil exchange pool isotope compositions when there is a significant uptake flux from deeper soils.

While the alkaline earth stable isotopes together have proven useful in demonstrating the role of nutrient biolifting across the Kohala climosequence, the Ba isotope system is clearly the most straightforward to interpret. The positive, site-specific relationships between τ_{Ba} and τ_{P} evident in Figure 5e suggest a mechanistic link between these two elements, P as the nutrient and Ba as the isotope proxy. We thus view Ba stable isotopes as a potentially powerful proxy for nutrient biolifting in other present day- and paleo-soil systems.

Conclusions

The fate of rock-derived nutrients such as P and Ca lies in a complex interplay between leaching that carries nutrients into groundwater and aquatic ecosystems and *in situ* biological use and effective recycling of those nutrients. Ultimately, the rate of nutrient release by weathering and its retention within ecosystems is determined by leaching power. To evaluate the chemical signature of ecosystem retention of nutrients, we took advantage of variable leaching power in a natural setting by sampling soils formed in same-aged volcanic (HVS) materials but residing in different climate zones along a soil climosequence on Kohala Mountain, Hawaii. Previous work along this climosequence had revealed enrichment of P in shallow relative to deeper soil horizons particularly at sites receiving intermediate MAP along the precipitation gradient. In this study the stable isotope compositions of exchangeable Ca, Sr and Ba in the soils were used to test the hypothesis that biolifting of P by plant roots from depth rather than deposition of P from atmospheric sources was mainly responsible for concentration of P at the surface. Positive site-specific relationships in mass gains/losses from the soils (τ values) between P and Ca, Sr and Ba provide evidence for a mechanistic link between these elements and allow the stable isotopes to be used as proxy tracers of P dynamics in these soils. As a novel approach and rather than assuming a single soil parent material, we used the Ti/Nb ratio which is both diagnostic of variability across the HVS compositional spectrum and a conservative ratio in the soils to link individual soil samples to a restricted range of HVS parent materials in order to obtain a robust assessment of inter-element τ relationships.

At sites along the climosequence 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 the range of compositions observed in the HVS parent materials. As the plant communities at these sites are stable (i.e. not aggrading or degrading),

model results reveal that this condition requires that the nutrient uptake flux from the shallow soils is less than the recycling flux through litterfall to those soils which implies an additional source of light isotopes as an uptake flux that we attribute to nutrient (and proxy) biolifting. Exchangeable Ca, Sr and Ba at these sites generally become isotopically heavier with depth, and for all sites along the climosequence soils at depth >10 cm have exchangeable Ba that is heavier than or at the heavy end of the isotopic range observed in the HVS parent materials. We view the isotopically heavy Ba on deeper exchange sites to represent the complement of the light fraction biolifted from these soils, and its persistence over the climosequence requires that the nutrient uptake flux from deep soils exceeds any recycling flux derived from leaching of shallow soils.

The fidelity of the Ba isotope signal of biolifting is due to the lesser susceptibility of Ba to leaching relative to that of Ca and Sr, the isotope profiles of which show evidence of downward transfer of a portion of the isotopically light biocycled fraction and thus a more gradual increase of heaviness with depth compared to the Ba isotope profiles. Even at sites where the composition of the soil exchange pool has been impacted by secondary mineral formation (e.g. carbonate formation) or land use change (e.g. deforestation and cattle grazing), the Ba isotope record of biolifting has persisted. Thus the Ba isotopes constitute the most robust indicator of nutrient biolifting and we suggest that the Ba isotopes by correlation are likely to provide a powerful tracer of the dynamics of P and other inorganic nutrients in soils elsewhere.

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1028 conclusions.

Figure Captions

Figure 1. Map of sampling sites on the ~150 ka Hawi lava flows along the Kohala climate gradient. Rainfall isohyets are derived from Giambelluca et al. (2012).

Figure 2. Comparison of chemical and isotopic measurements of water and subsequent exchange fractions of Kohala soils. Figure 2c is an expanded portion of Figure 2b shown by the dashed box. The 1:1 correlation lines are provided for visual reference.

Figure 3. Chemical variation diagrams for Hawi Volcanic Series samples. Data from Spengler and Garcia (1988) are for lavas, data for lava and tephra fragments are from the present study. Lines in each plot are calculated regressions through all the data; bars showing 2SE (2 times the standard error of the regressions) are shown for reference.

Figure 4. Ca, Sr and Ba isotope compositions of lava and tephra fragments analyzed for this study. In Figures 3a-3c, isotope compositions are plotted relative to Ti/Nb as a measure of magmatic evolution. In Figures 3d-3f, Ca, Sr and Ba isotope compositions are plotted relative to Nb/Ca, Nb/Sr and Nb/Ba respectively. Using this plotting format, mixtures of two end-members and “un-mixing processes” such as separation of crystals from liquid, form straight-line arrays. “Predicted plagioclase composition” in Figures 3d and 3e is at the intersection of the regression through the data and the vertical axis (i.e. at zero Nb/Ca, Nb/Sr).

Figure 5. Ti/Nb and tau data for the <2-mm fraction from six soil profiles along the Kohala climosequence; open symbols are for profiles at sites where P is enriched in surface soils relative to abundances in deeper soils, as shown in Figure 5b; solid symbols are for profiles that do not show evidence of P enrichment in shallow soils. Lines in Figures 5c-5e are 1:1 correlations between τ_P and τ_{Ca} , τ_{Sr} or τ_{Ba} to provide a visual reference for comparison. In Figures 5b-e a value $\tau=0$ indicates no net loss or gain of element mass relative to the parent

composition. In Figure 5f the losses/gains of Ca, Sr and Ba relative to those of P are plotted as a function of MAP, with site names given by the letters. The y-axis variable equates to $(\text{Ca}, \text{Sr}, \text{Ba}/\text{P})_{\text{sample}}/(\text{Ca}, \text{Sr}, \text{Ba}/\text{P})_{\text{parent}}$. A value of 1.0 on the y-axis corresponds to identical loss or gain of Ca, Sr, or Ba and P.

Figure 6: Ca, Sr and Ba isotope compositions of exchangeable fractions of soils from four sites.

Open symbols are for sites where P is enriched in surface horizons relative to abundances in deeper soils, closed symbols are for high MAP site L where P is not enriched in shallow horizons. The shaded band within each plot give the range of isotope compositions for HVS samples measured for this study. Values for seawater are shown for reference, data sources given in text. Horizontal labeled lines along the isotope axis give the values of roots (R), stemwood (S) and foliage (F) for an Ohi'a seedling collected from a recent lava flow on Hawaii. The isotope compositions of lava fragments attached to the roots (Table 2) lie very close to the heavy side of the HVS composition band in each diagram.

Figure 7: Ca and Ba isotope compositions of exchangeable soil fractions for two comparisons of soil profiles. The shaded band within each plot gives the range of isotope compositions for HVS samples measured for this study. Figures 7a-c show the comparison of two low-MAP sites showing the influence of pedogenic carbonate formation on the Ca isotope profile at site B, and the lack of an influence on the Sr and Ba isotope profiles. The dashed vertical line in Figure 7a shows the Ca isotope composition of a sample of pedogenic carbonate collected at site B. Figures 7d-f show the comparison of a deforested site (site M) and adjacent forested site (MF) showing the influence of disturbance/land use change on the Ca and Sr isotope profiles at site M, and the lack of an influence on the Ba isotope profile.

Figure 8: a) Box model describing Ca mass and isotope flux between shallow soil and deep soil exchangeable pools and vegetation, closely following that presented by Holmden and Belanger (2010). Variables, fluxes and equations used in the model scenarios are given in Table 6 included in this figure. b) Results of model scenarios described in the text. $\delta^{44/40}\text{Ca}$ is plotted relative to fresh lava which has an assumed value of 0‰ for purposes of the model.

Figure 9: Isotope compositions of exchangeable Ba for the shallowest sample at each site (“top 10 cm”) and for deeper samples (“below 10 cm”) calculated as a depth-integrated value using bulk density and sample thickness parameters from Chadwick et al. (2003). The band labeled “range of HVS parent materials” shows range of $\delta^{138/134}\text{Ba}$ for lava and tephra fragment samples analyzed for this study.

Table Captions

Table 1. Selected chemical and isotopic parameters for HVS lava and tephra fragment samples analyzed for this study.

Table 2. Summary of Ca, Sr and Ba concentrations and isotope compositions of tissues (roots, stem, foliage) for Ohi'a seedling sample collected from recent lava flow to the east of Kilauea Volcano, Hawaii and of lava fragments attached to the roots. Note that the Ca, Sr and Ba isotope compositions of the lava fragments are essentially identical to the heaviest lava and tephra fragments collected from the Kohala climosequence soils (Table 1).

Table 3. Isotope compositions of water leachable and exchangeable Ca, Sr and Ba in Kohala climosequence soils (<2 mm). For samples having both water and exchange fractions listed, the “total exchange pool” values are the sum of the individual operational fractions. Values for samples having the exchange fraction only are assumed to include the water leachable component in their total amounts.

Table 4. Chemical compositions (Ca, Sr, Ba concentrations) of water leach and exchangeable fractions of Kohala climosequence soils (<2 mm). For samples having both water and exchange fractions listed, the exchange procedure was performed on the residue of the water leach procedure. Values for samples having the exchange fraction only are assumed to include the water leachable component in their total amounts.

Table 5: Selected chemical parameters for <2-mm fractions of Kohala climosequence soils, with tau parameters as defined in text. Data were collected for study described in Chadwick et al. (2003) but not specifically discussed in that publication.

Table 6: Variables, mass fluxes and governing equations used in soil and vegetation pool box model presented in Figure 8. Initial condition and fluxes are shown for three model scenarios.

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Figure

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1.

	SiO ₂	Ti	Nb	P	Mg	Ca	Sr	Ba	δ ^{44/40} Ca	δ ^{88/86} Sr	^{87/86} Sr	δ ^{138/134} Ba
	Wt.%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	per mil	per mil		per mil
site B, lava	49.92	18130	56	8715	27966	51197	1715	644	0.97	0.24	0.70355	0.07
site B (0-10cm), tephra fragment	53.07	12211	93	6429	14372	26831	1183	1190	0.65	0.15	0.70372	-0.02
site B (10-20cm), tephra fragment	54.20	14145	104	6153	14216	17869	584	1125	0.37	-0.02	0.70378	0.03
site B (55-70cm), tephra fragment	54.83	11905	94	5626	13471	28559	1328	881	0.74	0.16	0.70361	-0.02
site E, lava	49.92	14079	70	7707	22578	46153	1692	767	0.97	0.27	0.70355	0.10
site I, tephra fragment	50.24	17886	70	8648	22365	33458	899	791	0.83	0.18	0.70357	0.07
site P, tephra fragment	50.74	15694	80	8331	20953	32360	1096	954	0.74	0.18	0.70359	0.03
site M, tephra fragment	51.20	16248	83	10357	19995	28710	677	842	0.69	0.10	0.70358	0.00

Table 2.

	Ca	Sr	Ba	Ca/Sr	Sr/Ba	$\delta^{44/40}\text{Ca}$	$\delta^{88/86}\text{Sr}$	$^{87/86}\text{Sr}$	$\delta^{138/134}\text{Ba}$
	ppm	ppm	ppm			per mil	per mil		per mil
Roots	1710	10.1	5.4	169	1.44	-1.08	-0.53	0.70541	-0.75
Stem	2540	9.6	5.1	265	1.88	-2.01	-0.30	0.70502	-0.48
Foliage	2940	4.2	2.5	700	1.68	-0.60	-0.12	0.70502	-0.20
Attached lava fragments	65714	418	201	157	2.08	+0.96	+0.24	0.70386	+0.08

Table 3.

site	depth (cm)	Water fraction:					Exchange fraction:				
		Ca	Sr	Ba	Ca/Sr	Sr/Ba	Ca	Sr	Ba	Ca/Sr	Sr/Ba
		cmol (+)/kg	cmol (+)/kg	cmol (+)/kg	molar	molar	cmol (+)/kg	cmol (+)/kg	cmol (+)/kg	molar	molar
B	0-10	0.275	0.0060	0.0004	45	13.91	6.90	0.1678	0.0356	41	4.71
	10-37	0.123	0.0083	0.0013	15	6.51	3.30	0.2152	0.1097	15	1.96
	37-65	0.156	0.0280	0.0021	6	13.21	4.06	0.7685	0.2881	5	2.67
	65-100	0.025	0.0028	0.0023	9	1.25	7.24	0.5273	0.3353	14	1.57
	100-138	0.049	0.0016	0.0000	31	33.24	2.72	0.0832	0.0105	33	7.91
E	0-13	-	-	-	-	-	11.73	0.1973	0.0300	59	6.58
	13-30	-	-	-	-	-	13.05	0.3124	0.0396	42	7.89
	30-44	-	-	-	-	-	11.78	0.3327	0.0718	35	4.64
	44-62	-	-	-	-	-	13.97	0.6355	0.0885	22	7.18
	62-85	-	-	-	-	-	12.87	0.5912	0.0579	22	10.21
	85-103	-	-	-	-	-	9.37	0.4205	0.0663	22	6.35
I	0-22	1.017	0.0149	0.0014	68	10.78	15.55	0.2314	0.0508	67	4.55
	22-38	0.813	0.0145	0.0011	56	12.85	16.39	0.3085	0.0939	53	3.29
	38-72	0.675	0.0144	0.0006	47	25.59	15.88	0.3954	0.1077	40	3.67
	72-85	0.339	0.0070	0.0001	48	65.22	15.89	0.3398	0.0809	47	4.20
	85-132	0.158	0.0018	0.0000	90	47.26	9.93	0.1029	0.0092	96	11.15
	132-175	0.155	0.0017	0.0000	90	102.14	9.54	0.1060	0.0041	90	25.86
J	0-22	-	-	-	-	-	1.32	0.0201	0.0038	66	5.33
	22-47	-	-	-	-	-	3.41	0.0769	0.0101	44	7.64
	47-67	-	-	-	-	-	3.31	0.0714	0.0097	46	7.38
	67-92	-	-	-	-	-	1.98	0.0627	0.0179	32	3.51
	92-125	-	-	-	-	-	3.16	0.2908	0.0268	11	10.86
	125-185	-	-	-	-	-	2.05	0.1056	0.0290	19	3.65

M	0-10	0.124	0.0011	0.0006	108	2.03	0.37	0.0039	0.0033	95	1.17
	10-28	0.076	0.0008	0.0002	92	3.52	0.23	0.0025	0.0014	92	1.80
	28-42	0.064	0.0025	0.0011	26	2.32	0.18	0.0079	0.0086	23	0.92
	42-58	0.039	0.0024	0.0014	16	1.76	0.13	0.0076	0.0151	17	0.50
	58-79	0.032	0.0012	0.0017	27	0.69	0.09	0.0033	0.0148	27	0.22
	79-101	0.046	0.0013	0.0049	36	0.26	0.15	0.0043	0.0729	36	0.06
	101-110	0.020	0.0005	0.0018	44	0.26	0.06	0.0014	0.0214	45	0.06
	110-120	0.012	0.0002	0.0001	61	2.89	0.03	0.0003	0.0005	78	0.62
	120-132	0.017	0.0002	0.0001	87	1.48	0.04	0.0004	0.0013	98	0.32
MF	0-5	0.715	0.0085	0.0013	84	6.44	0.36	0.0044	0.0009	81	4.67
	5-10	0.056	0.0006	0.0002	99	3.07	0.04	0.0004	0.0003	114	1.31
	10-15	0.041	0.0004	0.0002	98	2.46	0.04	0.0003	0.0003	125	1.25
	15-20	0.026	0.0002	0.0001	128	2.42	0.04	0.0003	0.0004	137	0.70
	20-25	0.032	0.0003	0.0001	121	2.62	0.04	0.0003	0.0004	137	0.75
	25-30	0.028	0.0002	0.0001	140	3.13	0.03	0.0002	0.0003	153	0.85
	30-40	0.019	0.0001	0.0000	157	3.90	0.03	0.0002	0.0001	180	1.07
	40-50	0.019	0.0001	0.0000	175	6.85	0.04	0.0003	0.0002	146	1.42
L	0-5	0.050	0.0003	0.0001	151	3.66	0.16	0.0011	0.0004	143	3.08
	5-10	0.016	0.0001	0.0001	156	1.64	0.06	0.0011	0.0003	58	3.94
	10-15	0.025	0.0001	0.0001	176	2.11	0.05	0.0004	0.0002	107	2.22
	15-20	0.011	0.0001	0.0000	128	1.94	0.02	0.0002	0.0002	105	1.45
	20-30	0.005	0.0000	0.0000	180	2.73	0.08	0.0003	0.0002	229	1.94
	30-40	0.020	0.0001	0.0001	135	1.93	0.10	0.0005	0.0004	184	1.24
	40-50	0.035	0.0003	0.0001	126	2.19	0.07	0.0002	0.0003	290	0.78
	50-60	0.033	0.0002	0.0001	154	2.70	0.10	0.0004	0.0003	227	1.33
	60-70	0.028	0.0003	0.0002	92	1.61	0.10	0.0005	0.0009	194	0.60
	70-120	0.038	0.0003	0.0004	140	0.72	0.14	0.0006	0.0018	253	0.31

Table 4.

site	depth (cm)	Water fraction:			Exchange Fraction:			Total Exchange Pool			
		$\delta^{44/40}\text{Ca}$	$\delta^{88/86}\text{Sr}$	$\delta^{138/134}\text{Ba}$	$\delta^{44/40}\text{Ca}$	$\delta^{88/86}\text{Sr}$	$\delta^{138/134}\text{Ba}$	$\delta^{44/40}\text{Ca}$	$\delta^{88/86}\text{Sr}$	$^{87/86}\text{Sr}$	$\delta^{138/134}\text{Ba}$
		per mil	per mil	per mil	per mil	per mil	per mil	per mil	per mil		per mil
B	0-10	0.32	0.12	-0.01	0.60	0.09	-0.04	0.59	0.09	(0.70407)	-0.04
	10-37	0.51	-	-	0.65	-0.01	0.35	0.64	-0.01	(0.70405)	0.35
	37-65	0.28	-0.09	0.34	0.55	-0.08	0.37	0.54	-0.08	(0.70401)	0.37
	65-100	0.88	-	-	0.60	0.05	0.31	0.60	0.05	(0.70396)	0.31
	100-138	1.29	0.29	0.29	1.11	0.32	0.28	1.11	0.32	(0.70391)	0.28
E	0-13	-	-	-	0.18	-0.09	-0.10	0.18	-0.09	0.70402	-0.10
	13-30	-	-	-	0.28	0.08	0.37	0.28	0.08	0.70403	0.37
	30-44	-	-	-	0.23	0.18	0.43	0.23	0.18	0.70400	0.43
	44-62	-	-	-	0.10	0.13	0.40	0.10	0.13	0.70397	0.40
	62-85	-	-	-	0.63	0.28	0.40	0.63	0.28	0.70392	0.40
	85-103	-	-	-	1.09	0.20	0.35	1.09	0.20	0.70388	0.35
I	0-22	-0.32	-0.16	-0.20	-0.37	-0.15	-0.19	-0.37	-0.15	0.70411	-0.19
	22-38	-0.05	-	-	0.14	-0.06	0.18	0.13	-0.06	0.70409	0.18
	38-72	0.42	-0.02	0.25	0.14	-0.04	0.23	0.15	-0.04	(0.70402)	0.23
	72-85	0.42	-	-	0.18	0.00	0.35	0.19	0.00	0.70402	0.35
	85-132	0.92	-	-	1.15	0.19	0.30	1.15	0.19	0.70398	0.30
	132-175	1.48	0.17	0.43	1.06	0.15	0.38	1.07	0.15	0.70392	0.38
J	0-22	-	-	-	-0.18	-0.12	-0.06	-0.18	-0.12	(0.70395)	-0.06
	22-47	-	-	-	0.11	0.06	0.27	0.11	0.06	(0.70390)	0.27
	47-67	-	-	-	0.52	0.03	0.29	0.52	0.03	(0.70388)	0.29
	67-92	-	-	-	0.64	-0.02	0.09	0.64	-0.02	(0.70386)	0.09
	92-125	-	-	-	1.02	0.18	0.16	1.02	0.18	(0.70379)	0.16
	125-185	-	-	-	0.85	0.13	0.31	0.85	0.13	(0.70380)	0.31

Table 5.

site	depth (cm)	Ti ppm	Nb ppm	P ppm	Ca ppm	Sr ppm	Ba ppm	Ti/Nb	P/Nb _p	τP	Ca/Nb _p	τCa	Sr/Nb _p	τSr	Ba/Nb _p	τBa
B	0-10	22380	96	2884	4141	272	561	233	121	-0.75	656	-0.93	23	-0.88	11	-0.49
	10-37	23940	118	1967	2356	246	494	203	105	-0.84	567	-0.96	20	-0.90	11	-0.62
	37-65	21300	143	1835	3070	556	758	149	76	-0.83	409	-0.95	15	-0.74	10	-0.48
	65-100	18420	131	2972	7069	570	834	141	71	-0.68	384	-0.86	14	-0.70	10	-0.37
	100-138	12660	99	2272	22063	1647	889	128	64	-0.64	347	-0.36	13	0.25	10	-0.09
E	0-13	20640	77	5594	10282	372	596	268	140	-0.48	758	-0.82	26	-0.81	12	-0.35
	13-30	22500	82	3627	8068	428	650	274	143	-0.69	776	-0.87	27	-0.80	12	-0.34
	30-44	22740	90	2404	5998	359	623	253	132	-0.80	713	-0.91	25	-0.84	12	-0.41
	44-62	23640	82	1879	6283	638	545	288	151	-0.85	817	-0.91	28	-0.72	12	-0.45
	62-85	25260	96	2098	6212	695	476	263	137	-0.84	743	-0.91	26	-0.72	12	-0.58
	85-103	25080	103	1792	5569	470	518	243	127	-0.86	686	-0.92	24	-0.81	12	-0.56
I	0-22	13980	41	16125	17779	979	1657	341	179	1.19	972	-0.55	33	-0.27	13	2.14
	22-38	22200	70	10707	10639	658	1301	317	167	-0.08	902	-0.83	30	-0.69	13	0.48
	38-72	22320	86	10663	7211	557	1307	260	135	-0.08	733	-0.89	25	-0.74	12	0.29
	72-85	22740	70	4851	8354	531	643	325	171	-0.59	924	-0.87	31	-0.76	13	-0.27
	85-132	21480	111	4326	7925	266	238	194	100	-0.61	539	-0.87	19	-0.88	11	-0.80
	132-175	22140	109	6205	7925	293	100	203	105	-0.46	568	-0.87	20	-0.87	11	-0.92
J	0-22	21120	63	11755	8996	432	709	335	176	0.06	955	-0.85	32	-0.79	13	-0.12
	22-47	28860	85	6730	6283	331	426	340	179	-0.56	967	-0.92	33	-0.88	13	-0.61
	47-67	24900	92	5812	5212	328	290	271	141	-0.55	766	-0.93	26	-0.86	12	-0.74
	67-92	23100	60	6642	7925	706	646	385	203	-0.45	1101	-0.88	37	-0.68	13	-0.20

92-125	22320	90	7079	7283	1359	713	248	129	-0.39	699	-0.88	24	-0.38	12	-0.32
125-185	22080	85	6642	5855	805	782	260	136	-0.42	734	-0.91	25	-0.63	12	-0.22

M	0-10	36600	101	3321	1214	49	325	362	191	-0.83	1034	-0.99	35	-0.99	13	-0.76
	10-28	37560	112	3278	1000	46	422	335	176	-0.83	955	-0.99	32	-0.99	13	-0.71
	28-42	33900	116	3321	1571	58	443	292	153	-0.81	829	-0.98	28	-0.98	12	-0.69
	42-58	31440	109	3889	1142	55	225	288	151	-0.76	818	-0.99	28	-0.98	12	-0.83
	58-79	33240	136	5069	1000	57	418	244	127	-0.71	689	-0.99	24	-0.98	12	-0.73
	79-101	27900	114	10226	2999	33	375	245	127	-0.30	690	-0.96	24	-0.99	12	-0.71
	101-110	31500	194	5506	714	34	370	162	83	-0.66	448	-0.99	16	-0.99	10	-0.82
L	5-11	35640	180	5288	1285	34	10	198	102	-0.71	553	-0.99	20	-0.99	11	-0.99
	11-16	44460	204	9396	1000	32	10	218	113	-0.59	611	-0.99	21	-0.99	11	-1.00
	16-25	40440	215	10881	643	30	10	188	97	-0.48	524	-0.99	19	-0.99	11	-1.00
	25-40	24420	136	11799	1000	23	10	180	92	-0.06	499	-0.99	18	-0.99	11	-0.99
	40-56	26520	109	14334	2356	34	10	243	127	0.04	685	-0.97	24	-0.99	12	-0.99
	56-73	26280	113	13853	643	18	10	233	121	0.01	654	-0.99	23	-0.99	11	-0.99
	73-100	27240	138	11668	428	10	10	197	102	-0.17	551	-0.99	20	-1.00	11	-0.99
	100-109	24060	124	8216	428	12	10	194	100	-0.34	541	-0.99	19	-0.99	11	-0.99
	109-118	43320	300	6249	428	39	189	144	73	-0.72	396	-1.00	15	-0.99	10	-0.94

M	0-10	0.23	-0.09	-0.08	0.23	-0.09	-0.10	0.23	-0.09	(0.70749)	-0.10
	10-28	0.32	-	-	0.46	0.07	0.13	0.43	0.07	(0.70775)	0.13
	28-42	0.51	-	-	0.32	-0.02	0.15	0.37	-0.02	(0.70669)	0.15
	42-58	0.46	-	-	0.42	0.09	0.11	0.43	0.09	(0.70627)	0.11
	58-79	0.65	0.19	0.18	0.23	0.14	0.09	0.34	0.15	(0.70630)	0.10
	79-101	0.09	-	-	0.18	0.11	0.14	0.16	0.11	(0.70605)	0.14
	101-110	0.18	-	-	0.51	0.20	0.24	0.43	0.20	0.70595	0.24
	110-120	0.69	-	-	1.29	0.23	0.10	1.11	0.23	0.70586	0.10
	120-132	0.78	0.25	0.15	0.97	0.28	0.21	0.92	0.27	0.70585	0.20
MF	0-5	0.28	-0.09	-0.05	0.18	-0.12	-0.05	0.25	-0.10	0.70753	-0.05
	5-10	0.92	-	-	0.97	0.10	0.00	0.94	0.10	0.70763	0.00
	10-15	0.60	-	-	1.15	0.23	0.15	0.88	0.23	0.70761	0.15
	15-20	0.65	0.23	0.08	1.06	0.21	0.10	0.89	0.22	0.70772	0.10
	20-25	0.78	-	-	0.83	0.22	0.15	0.81	0.22	0.70782	0.15
	25-30	0.89	-	-	1.06	0.26	0.09	0.99	0.26	0.70711	0.09
	30-40	1.06	-	-	0.74	0.19	0.10	0.87	0.19	0.70661	0.10
	40-50	1.34	0.22	0.08	1.06	0.21	0.06	1.15	0.21	0.70638	0.06
L	0-5	1.02	0.35	-0.14	1.38	0.34	-0.15	1.30	0.35	0.70832	-0.15
	5-10	1.48	-	-	1.80	0.38	-0.11	1.73	0.38	0.70828	-0.11
	10-15	1.48	-	-	1.66	0.28	-0.07	1.60	0.28	0.70832	-0.07
	15-20	0.88	-	-	1.29	0.27	-0.09	1.16	0.27	0.70832	-0.09
	20-30	1.60	-	-	1.43	0.31	-0.05	1.44	0.31	0.70838	-0.05
	30-40	1.52	0.42	0.03	1.94	0.39	0.00	1.87	0.40	0.70841	0.00
	40-50	1.43	-	-	1.85	0.38	-0.03	1.71	0.38	0.70840	-0.03
	50-60	1.43	-	-	1.43	0.34	-0.02	1.43	0.34	0.70849	-0.02
	60-70	1.29	-	-	1.20	0.25	0.07	1.22	0.25	0.70852	0.07
	70-120	1.66	0.20	0.07	1.29	0.22	0.06	1.37	0.21	0.70865	0.06

Table 6

<u>Variables</u>	<u>Description</u>	<u>Model Scenario Initial Conditions</u>		
		I	II	III
M_{ss}	mass of exchangeable Ca in shallow soil	10	2000	2000
M_{ds}	mass of exchangeable Ca in deep soil	1000	1000	1000
M_{veg}	mass of Ca in vegetation	90	90	1900
X	fraction of plant uptake from shallow soil	0	1	0.5
δ_{ss}	$\delta^{44/40}\text{Ca}$ of shallow soil exchangeable Ca	-1.60‰	-0.84‰	+0.76‰
δ_{ds}	$\delta^{44/40}\text{Ca}$ of deep soil exchangeable Ca	+0.22‰	+1.76‰	+0.40‰
Δ_{veg}	$\delta^{44/40}\text{Ca}$ of vegetation	-2.00 ‰	-0.67‰	-1.81‰
δ_{lf}	$\delta^{44/40}\text{Ca}$ of recycled Ca (litterfall)	-1.60‰	-0.27 ‰	-1.41‰
δ_{gw}	$\delta^{44/40}\text{Ca}$ of Ca lost to groundwater	-	+1.76‰	+0.40‰
δ_a	$\delta^{44/40}\text{Ca}$ of atmospheric deposition	0‰	0‰	0‰
δ_w	$\delta^{44/40}\text{Ca}$ of Ca from mineral weathering	0‰	0‰	0‰
Δ_{uptake}	Fractionation factor during plant uptake	-2‰	-2‰	-2‰

Fluxes (mass units each model step)

f_u	plant uptake	2	2	0.2
f_{lf}	litterfall	2	0.2	2
f_a	atmospheric deposition	0	2.8	1.1
f_z	leakage from shallow soil	0	1	3
f_w	mineral weathering	2	1	0
f_{gw}	loss to groundwater	0	2	2.9

Equations (describe change each model step)

$$\Delta M_{ss} = f_a + f_{lf} - f_z - Xf_u \quad ; \quad \Delta(M_{ss}\delta_{ss}) = f_a\delta_a + f_{lf}\delta_{lf} - f_z\delta_{ss} - Xf_u(\delta_{ss} + \Delta_{uptake})$$

$$\Delta M_{ds} = f_w + f_z - f_{gw} - (1-X)f_u \quad ; \quad \Delta(M_{ds}\delta_{ds}) = f_w\delta_w + f_z\delta_{ss} - f_{gw}\delta_{ds} - (1-x)f_u(\delta_{ds} + \Delta_{uptake})$$

$$\Delta M_{vegetation} = f_u - f_{lf} \quad ; \quad \Delta(M_{vegetation}\delta_{vegetation}) = Xf_u(\delta_{ss} + \Delta_{uptake}) + (1-x)f_u(\delta_{ds} + \Delta_{uptake}) - f_{lf}\delta_{lf}$$

Note: this table is to be incorporated in Figure 8