UC Santa Barbara

UC Santa Barbara Electronic Theses and Dissertations

Title

Strontium Isotopes Fingerprint Base Cation Sources During Early-Stage Soil Formation on Hawaiian Basalt Flows

Permalink

https://escholarship.org/uc/item/3k9127w3

Author

Bingham, Nina Lynn

Publication Date

2015

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA

Santa Barbara

Strontium Isotopes Fingerprint Base Cation Sources During Early-Stage

Soil Formation on Hawaiian Basalt Flows

A Thesis submitted in partial satisfaction of the

requirements for the degree Master of Arts

in Geography

by

Nina Lynn Bingham

Committee in charge:

Professor Oliver Chadwick, Chair

Professor Matthew Jackson

Professor Bodo Bookhagen

December 2015

The thesis of Nina Lynn Bingham is approved.

_____

Bodo Bookhagen

_____

Mathew Jackson

_____

Oliver Chadwick, Committee Chair

December 2015

Acknowledgements

To my advisor, Oliver Chadwick, for agreeing to let me do this project on top of another, actually funded project and guiding me through the process with not only great enthusiasm, but patience too. To Matt Jackson, who is responsible for my knowledge of isotope systems and has been so excited by the application of isotopes to the soils system. To Bodo Bookhagen, who has graciously supported this endeavor and provided direction to my graduate career. To Katherine Maher at Stanford University for allowing me the opportunity to work in her lab and to Karrie Weaver for guiding me through the analyses. To my friends and family, for always being there. I am lucky to be surrounded by friends, family and colleagues who enable me to pursue what I love, thank you all!

Abstract

Strontium Isotopes Fingerprint Base Cation Sources During Early-Stage

Soil Formation on Hawaiian Basalt Flows

by

Nina Lynn Bingham

Soil residence times for dynamic landscapes are often relatively short compared to geologic timescales. The nutrient status of these soils is controlled by the rates of chemical and physical rock weathering and soil development. Studies which constrain most external soil forming factors produce translatable results to more complicated systems, providing a baseline interpretation of incipient soil development. Therefore, I seek to understand soil formation over a relatively short time scale (0 to 7500 years) through the sourcing of plant available base cations by measuring the strontium (Sr) isotopic composition of the soil exchange complex and residual soil pools in a young, tropical chrono-climosequence. Our sampling strategy spans soils in three different precipitation ranges (950-1060 mm, 1180-1210 mm, and 1450-1500) and an array of soil ages from 500 to 7500 years in the Kona region on the island of Hawaii. In Hawaiian soils, $^{87}Sr/^{86}Sr$ values are determined by a mixture of three components: a mantle-derived component from the lava (0.7034, Kennedy et al., 1998), a rainfall component (0.7093, Kennedy et al., 1998) and a component from continental dust (0.720, Nakai et al., 1983; Kennedy et al., 1998). In contrast to the clear-cut differentiation in Sr isotopes with precipitation shifts observed in older soils, patterns on these young soils in Kona are complicated by low soil water residence times and small

surface to volume ratios for the rock. This kinetic constraint to rock weathering is implied by the low proportion of bulk Sr compared to that of its rock substrate. The low concentrations of bulk Sr in the soil enables detection of dilute atmospheric Sr fluxes on the soil Sr isotope signatures. Precipitation is a driving factor controlling the proportion of atmospheric influence. In the driest sites, where leaching intensity is dramatically reduced, there is a buildup of rainfall-derived extractable Sr in the soil over time on top of the small supply of cations from rock weathering. Thus, extractable Sr isotope signatures reflect both the input of rainfall-derived cations and rock-derived cations with values that fall between rainfall and basaltic signatures. Sr isotopes and mixing model results point towards increased rock weathering in the wettest localities. However, elevational driven increased precipitation intensity leads to increased soil leaching at some sites which depletes the concentration of base cations supplied by basalt and a dilute resupply of cations by rainfall is apparent in the Sr isotope values. Soils in the intermediate precipitation range have Sr isotopic signatures consistent with both the wet and dry trends; suggesting that they lie close to the critical precipitation amount that marks a shift between these two processes. For the Kona region, this transition seems to occur at 1200 mm /yr. Finally, kinetic limitation to rock weathering allows dust accumulation, although small, to be detectable in the Sr signature for residual soils.

TABLE OF CONTENTS

1. Introduction

The balance between chemical and physical weathering rates of rock and its impact on soil nutrient status evolves as soils develop (Gabet et al., 2015; Amundson et al., 2015). This balance is a function of soil residence time (Heimsath, 2012), which is controlled by topographic position, tectonic forcing and climate setting (Dixon and Riebe, 2014). Soils with residence times $>\sim10^5$ years are rare in many parts of the continents because of the dynamic nature of tectonics and climate change. Evaluating the effects by multiple external factors on soil development is not easy because in many settings there is a lack of clear separation among possible control variables. Simple landscape settings, which exclude topographic influence and where age (climosequence) and climate conditions (chronosequences) can be constrained, set a baseline for soil development in the context of climate and soil age as seen by marine and fluvial terrace soil research (Jenny, 1973; Maher et al., 2009). Targeting younger soils within chronosequences and climosequences allows a detailed evaluation of soil development and soil nutrient status in the soil residence time range of more dynamic soils on slopes.

The Hawaiian Islands provide a unique natural laboratory where basaltic soil development and its impact on soil fertility can be studied under orthogonal gradients of climate and substrate age that provide state factor constraints (ie: minimizing variations in one or more of these external influences: climate, parent material, relief, organisms and time) to better understand pedogenic and ecosystem processes, without the influence of topography (Jenny, 1941; Vitousek, 2004). The islands offer a temporally constant but spatially varied rainfall pattern overlaid onto basaltic shield lava derived soils ranging in age from essentially 0 to over four million years. In Hawaii, Polynesian agricultural expansion

1

across the islands maps onto fertile areas, defined by the availability of alkaline earth and alkali cations and phosphorus (Ladefoged et al., 2009). In contrast to soils beginning to develop on fresh rock, soils developed on highly weathered rock can be depleted in soil nutrients due to complete primary mineral depletion and long-term leaching of the weathering products (Chadwick et al., 1999). The primary store of these ions is derived from rock minerals during weathering of lava and tephra as soils develop. Thus, if these ions are not released quickly enough by weathering or if they have been leached too rapidly by excess moisture, other sources such as rainfall or exogenous dust can play significant roles in providing the needed nutrients (Kennedy et al., 1998; Chadwick et al., 1999; Stewart et al., 2001; Kurtz et al., 2001).

Fine-grained material settling in the cracks of cooling a'a lava or by gradual accumulation on top of the less fractured pahoehoe flows initiates basaltic soil formation. The locally derived tephra and plant material become trapped in these crevices and, with sufficient rainfall, pioneering plants begin to grow (Lincoln et al., 2014). Kinetic limitation on the weathering rate of the fresh lava is likely in this environment due to low surface area lava cobbles (clinkers) and fast hydrologic flow through large macropores between the cobbles (Clow and Drever, 1996; White and Brantley, 2003; Brantley et al., 2008). Thus, it is likely that this initial soil is dominated by accumulation of organic matter and/or local dust derived from organic matter-rich material (Porder et al., 2007). If soluble cations are available, the organic matter provides charged surfaces to sorb them. However, the cation exchange capacity of the organic matter may remain unfilled by base (non-hydrolyzing) cations due to the potentially low release rate of rock derived base cations. Thus, it is possible that although the rocks have high concentrations of cations, the soil exchange may

have a low base saturation. This condition would be quite different than the low base saturation described in previous studies for older, wet Hawaiian soils (Kennedy et al., 1998; Chadwick et al., 2003; Chadwick et al., 2009). The interplay between the rate of base cation production by rock weathering and the removal of base cations by soil leaching controls the fraction on the exchange complex (balanced against acid cations – H^+ and Al^{3+}) for these incipient soils.

The objective of this research is to determine the source and dynamics of soil base cation pools during early pedogenesis. In particular, I use Sr isotopes ($^{87}Sr/^{86}Sr$) to evaluate sources of plant-available cations and compare those sources to the background amount of cations that have not yet been released to available forms. Although it may seem that the existing exchange complex in young soils should be dominated by rock-derived cations, it is possible that the limited surface area available for weathering may limit release of cations even as they are being added from external dust/rainfall sources. These balances are poorly constrained in recently weathered soils.

2. Background

2.1 Base saturation trends for Hawaii

In Hawaii, the changing patterns of base saturation (the proportion of non-hydrolyzing cations in a soil to the cation holding capacity of a soil) over very long timescales and broad precipitation ranges have been defined previously by Chadwick and others (1999, 2009). Relatively young and/or dry soils, what would be putatively considered "unweathered," have high concentrations of base cations (Ca, Mg, Na, and K) and measurements of base saturation between 70 and 100%. The high base saturation is maintained for 10^4 years even under moderate to high precipitation amounts, but eventually

3

the minerals containing cations are depleted and the soil's acid buffering capacity declines. At this point, small increases in precipitation and/or soil age allow soil leaching to deplete base cations in the soil to very low levels (<10%) (Kennedy et al., 1998; Chadwick et al., 2003; Chadwick et al., 2009; Vitousek and Chadwick 2013).

Base saturation can be used as a proxy for soil fertility. In Hawaii, dryland agriculture systems are constrained by soil fertility. Vitousek et al. (2004) noted that expansion of dryland agriculture in the Kohala field system of Hawaii was limited to areas with base saturations higher than 30% and exchangeable Ca higher than 10 cmol$_c$/kg (Vitousek et al., 2004; Vitousek et al., 2013). Spatial models using the Vitousek et al. (2004) soil fertility parameters concur with archeological evidence of historic agricultural land all across the Hawaiian Archipelago; this agreement further demonstrates the applicability of base saturation and base cation metrics for determining fertile soils (Ladefoged et al., 2009). Beyond the clear patterning in the soil fertility data on the Hawaiian Islands, various isotope tracer systems have been utilized to identify the source of base cations as soils develop, providing a clear window into the processes behind the observed trends as detailed below.

2.2 Isotopes and trace elements applied to the Hawaiian ecosystem

Strontium (Sr) isotopes are useful in identifying sources of base cations in soil as Sr readily substitutes for calcium (Ca) in plagioclase feldspar (and other minerals) and Ca is often the dominant cation in the exchangeable group (Capo et al., 1998). On geologic timescales, rubidium-87 (Rb) decays to strontium-87, growing the pools of ^{87}Sr in the crust and mantle over time. Melting events in the mantle to form continental crust (CC), mid ocean ridge basalts (MORBs), or ocean island basalts (OIBs) fractionates the parent from the daughter in different proportions, which over time produces differences in the ^{87}Sr/^{86}Sr

ratio (^{86}Sr is a stable, non-radiogenic isotope of Sr) (Hofmann, 1997). The geologically long half-life of ^{87}Rb ($t_{1/2}$ = 48.8 Ga) provides relatively constant ^{87}Sr/^{86}Sr signatures on shorter, more ecologically relevant timescales (<100Ka) for the different sources of Sr (Capo et al., 1998). The end members can be used in mixing models to identify the origins of Sr (and other base cations) in the soil.

In Hawaii, the Sr isotopes associated with plant-available Sr, or extractable Sr, found in soils and in plant leaves are able to identify the source of base cations available as nutrients for plants (Kennedy et al., 1998). Hawaii is an isolated island, subjected to two major sources for Sr (and consequently base cations): mantle derived basalt (^{87}Sr/^{86}Sr = 0.7035) and seawater derived rainfall (^{87}Sr/^{86}Sr = 0.7092), and a minor source of Sr: Asia derived dust (^{87}Sr/^{86}Sr = 0.715-0.720) (Kennedy et al., 1998; Nakai et al., 1993). Comprehensive Sr isotope analysis of Hawaiian plants and soil, and the Hawaiian Sr endmembers (rock and atmosphere sources) broadly explains soil base saturation dynamics across Hawaii. In localities experiencing fast rock weathering rates, rock derived base cations dominate a high soil base saturation and the low ^{87}Sr/^{86}Sr signatures of the extractable Sr reflect this rock derived source of cations. In areas with increased soil leaching, soil base cations are depleted and the base saturation declines: high ^{87}Sr/^{86}Sr signatures of the extractable Sr reflect a small remaining pool of cations resupplied by the dilute source in rainfall (Kennedy et al., 1998; Chadwick et al., 2009).

In Hawaii, dust deposition and subsequent dust weathering plays an important role in resupplying elements susceptible to leaching losses, especially for older, highly weathered soils. In previous studies, bulk soil Sr (Sr for <2 mm soil, extractable Sr + residual soil Sr) 10 ka or older showed dust accumulation in the soil profile as identified by the soil Sr

isotope signatures (Chadwick et al., 1999; Kurtz et al., 2001; Chadwick et al., 2009). In addition to Sr isotopes, neodymium (Nd) isotopes, and rare earth element (REE) concentrations are useful for identifying continental dust accumulated in surface horizons of Hawaiian soils. Soils with Sr isotope values higher than the marine derived rainfall signature of 0.7092 are dust affected; use of Nd isotopes and REE ratios enables quantification of dust influence on these soils (Kurtz et al., 2001). Much like the Sr system, ε_{Nd} signatures ($\varepsilon_{Nd} =$

$$\left[\frac{\frac{143Nd}{144Nd}_{sample}}{\frac{143Nd}{144Nd}_{CHUR}} - 1 \right] * 10000,$$ where CHUR is the Chondritic Uniform Reservoir) are unique on

short timescales and can be associated with different sources of Nd to an ecosystem (ie: continental rock vs. MORB or OIB). Basalt-derived soils have Nd signatures between ε_{Nd} = 6 and ε_{Nd} = 8, whereas those affected by continental dust have ε_{Nd} values in surface horizons as low as -7. Additionally, leached soils that are not dust affected exhibit increases in the Sr isotope ratio but not in the ε_{Nd} values, as seawater supplies Sr but not Nd to local rainwater (Kurtz et al., 2001). Rare-earth element anomalies in the crust provide additional information for dust inputs and potential weathering indices that could be useful for deeper understanding of early soil formation. Chadwick et al. (1999) used the europium (Eu) anomaly to produce a second mixing model to verify Sr-Nd mixing dynamics for dust additions to soils. Europium is lower than expected in continental material as compared to other REEs of similar size and compatibility; thus, lower $Eu_{actual}/Eu_{expected}$ ratios indicate continental material mixing into soils originally derived from mantle-derived basalt (Chadwick et al., 1999). Kurtz et al. (2001) determined relative mobility differences between heavy rare earth elements (HREE) and light rare earth elements (LREE) in soil; HREEs tend to be more easily leached from the soil profile (Kurtz et al., 2001). Although

6

not included in this study, rare earth ratios and isotopes may be very useful to evaluate dust influence during initial soil formation.

2.3 Current understanding of early-stage soil development, complications

Much of the previous work on Hawaii has spanned long timescales and large climate gradients, providing a wide-view understanding of soil development processes on tropical volcanic islands in the Pacific Ocean. A focused look at the "unweathered" side of the soil development spectrum shows that despite their agricultural importance, only a few studies have attempted to discern soil development and ecosystem processes exclusively for the young soils on Hawaii (Vitousek et al., 1999; Lincoln et al., 2014). These soils often have mixed initial parent materials (tephra, plant debris, locally derived dusts, etc.), which make it difficult to identify specific sources of plant nutrients. In addition, the soil nutrient patterns are complicated simply by nature of the time allowed for soil development on shield surfaces – long time scales, on the order of hundreds of thousands to millions of years tends to dampen variability associated with different amount and size of rocks in the underlying lava flows and different amounts of tephra infiltrated into the voids associated with the rocks. Determining nutrient sources in heterogeneous soils forming recent lava flows (10^2 to 10^3 yr old) is likely to produce patterns that show both lower overall range in values and greater local variation than in soils on older lava flows (Porder et al., 2007; White et al., 1998).

Young lava flows are composed of rock and void space which can trap local dust that may be rich in organic matter and plant nutrients, but the resulting soil contains large relatively unweathered rock fragments colloquially known as "clinkers". In addition, soil depth is highly variable and often shallow (5-10 cm thick) making it difficult to sample fine-

grained soil material. To get around lack of soil on some of these young lava flows,

Vitousek et al., (1999) analyzed leaves from the widespread tree *Metrosideros polymorpha*

to understand plant nutrient sourcing on 100-300 and 2000-3000 year old soils on a range of

elevations, distances from the ocean and rainfall. Plants access the labile pool of soil cations

for nutrients and the Sr isotopic signatures of plants and the soil labile pool track each other

closely (Vitousek et al., 1999). Vitousek and others (1999) found that while most of the

plant leaves exhibited rock-derived Sr isotopic signatures, in the wettest localities a large

portion of the Sr in plant leaves was contributed by atmospheric sources. Additionally, they

found that annual precipitation, lava flow texture type (a'a vs pahoehoe) and distance from

the ocean explained most of the differences in Sr isotope signatures (Vitousek et al., 1999).

  More recently, Lincoln and others (2014) developed a chrono/climosequence (Figure

1) in the Kona region for the purpose of understanding patterns of nutrient status and how

that may have influenced pre-contact dryland agricultural expansion. Situated on the western

coast of the island of Hawaii, the soils span annual precipitation values between 800 and

1600 mm and lava flow ages between 500 and 7500 years. Lincoln et al. (2014) identified

several trends (Figure 2) for soil nutrients across this time-climate matrix, including a

decline in base saturation with increasing rainfall on all ages of substrate, and peaks in soil

fertility at the oldest and driest sites within the study area. Discerning the origins of plant

nutrients were beyond the scope of that study, but understanding changes in nutrient supply

and their sources for the Kona soils would add an important dimension to our interpretation

of soil development and nutrient supply across the Hawaiian Islands. Additionally, use of Sr

isotopes to study the relatively subtle soil cation dynamics on a comprehensive suite of

young soils would be the first of its kind. Here we seek to more fully understand soil

8

nutrient trends and inferred rock weathering patterns on these young soils using Sr isotope

measurements on rock, whole-soil (<2 mm) and ammonium acetate extractable Sr to detect
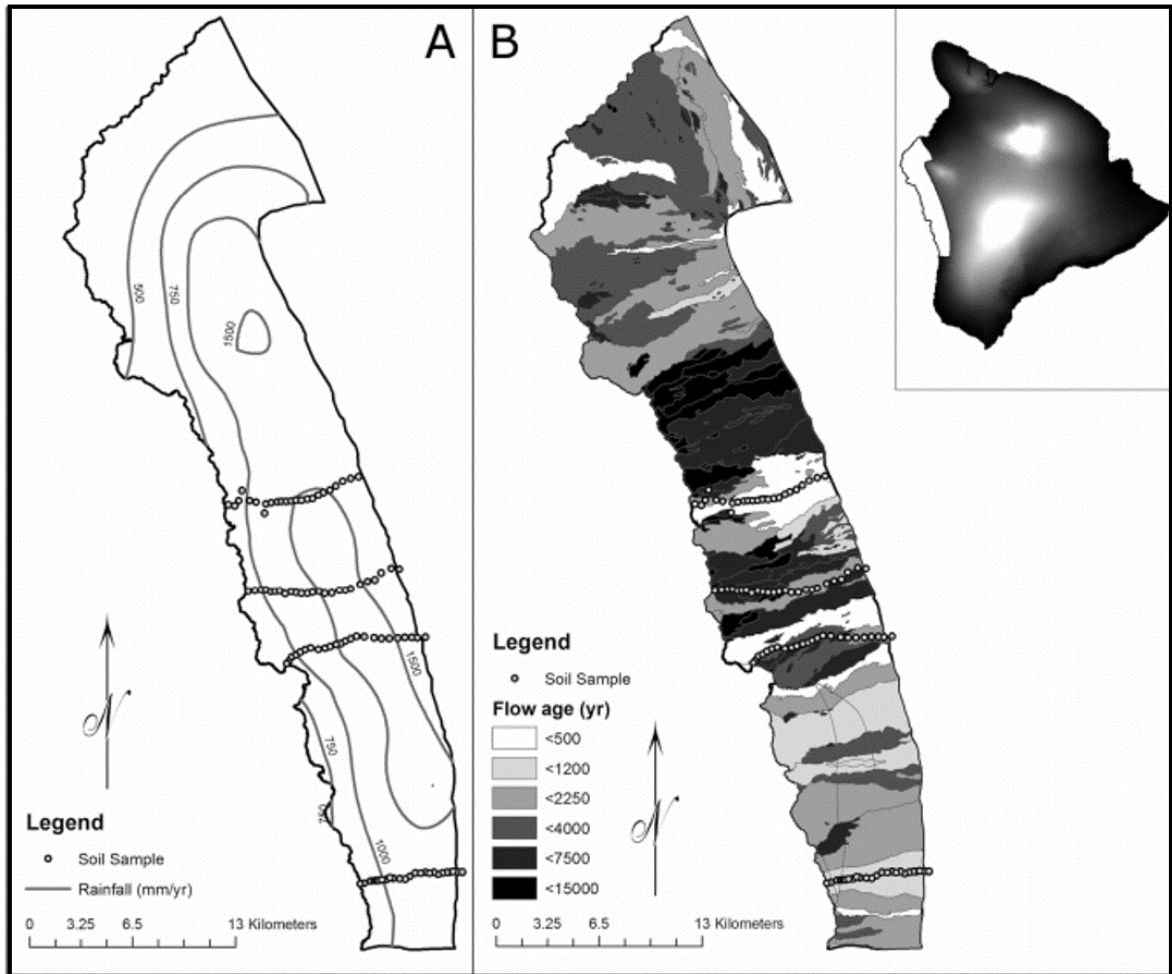
base cation sources.

Figure 1. All soil sampling locations overlaid onto base maps of annual precipitation (a) and lava flow age (b). Selected soil samples from those depicted above were analyzed for strontium isotopes in this study. Figure originally published in Lincoln et al., 2014.
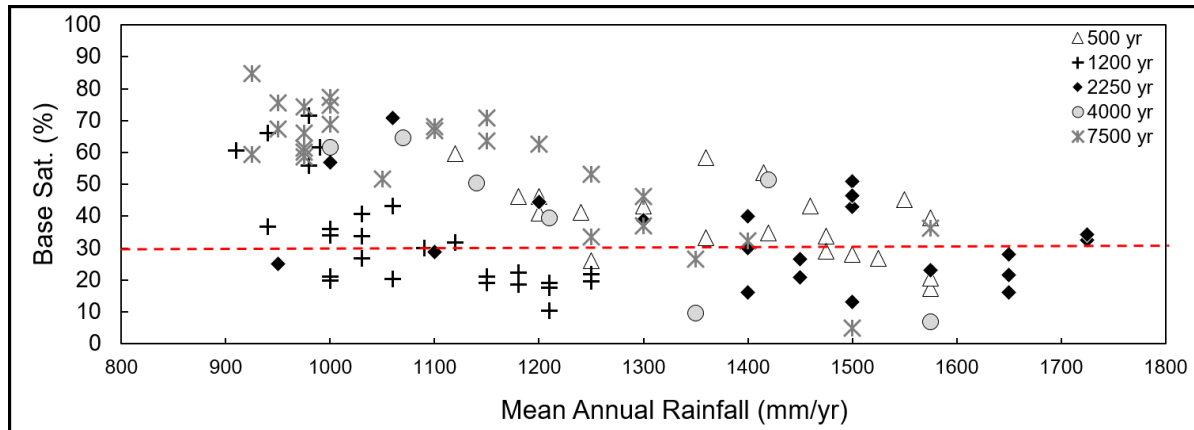
Figure 2. Base saturation for the young Kona soils compared to respective sample site annual rainfall. Flow age for each soil is denoted by a separate icon. Using 30% base saturation as a soil fertility indicator: points above the red dashed line are considered acceptable for agriculture, whereas points below are less suitable for agriculture. Soil fertility decreases with increasing rainfall. Older soils tend to have higher soil fertility than younger soils. This figure is reproduced from Lincoln et al., 2014.

3. Hypothesis

The observed decline in base saturation with increasing rainfall across the Kona region (Figure 2) could be produced when the cations from exchange sites equilibrate with leaching waters. Likely, the production of soil base cations by rock weathering cannot keep pace with the increased soil leaching associated with higher rainfall amounts. Based on previous base cation source studies (Kennedy et al., 1998, Chadwick et al., 1999), I expect the dilute but constant source of base cations from rainfall to become an important contributor of cations in these more heavily leached soils. The Sr isotopes in these soils should reflect the changing balance of base inputs and therefore move toward the rainfall endmember (0.7092). Contrasting the leaching effects on the soil, rock weathering should also produce changing patterns in base saturation in the young Kona climo-chronosequence. The older soils (7500 and 4000 yr) tend to have higher base saturations and show a less pronounced decline with increasing rainfall compared to the younger soils (1200 and 2250 yr). The trend suggests an increase in rock weathering with increasing soil age. I expect the

Sr isotopes to strongly reflect a basalt signature (0.7035) in samples where rock weathering contributes significant base cations to the soil exchange. Although these predictions of how base saturation and Sr isotopic signatures should respond to weathering and rainfall input differences, soil properties on recent lava flows are quite variable due to differences in initial conditions and may be sensitive to the nature of rainfall input and its proximity to the coast and oceanic contributions of cations via rainfall.

4. Methods

4.1 Sampling location characteristics

Aggregated 0-30 cm soil samples were taken in triplicate from the Kona District on the western coast of the island of Hawaii as described by Lincoln et al (2014). Sampling spanned a climate gradient from 900 to just over 1700 mm of precipitation annually and an age gradient encompassing lavas from 500 to 7500 years old (Figure 1) (Lincoln et al 2014). In contrast to much of Hawaii, rainfall maximums in Kona occur during the late afternoon of the summer months. Blocked by Mauna Loa and Haulalai, the persistent East-Northeast trade winds curl around the edges of these volcanoes and return to the Kona coast as onshore sea breezes, bringing with them moist air. Added land surface heating during afternoons (and especially in the hot summer months), moves the moist air upslope until convective clouds form at the lifting condensation level (LCL) and rainfall is possible (Leopold, 1949: Giambelluca, 1986). Surface heating drives the LCL to its highest level, 600 m, during the late morning; but, with the continued addition of moist air by the sea breeze, the surface temperature drops as does the LCL and rainfall is prevalent across the whole region (Yang and Chen 2003). With increasing rainfall, vegetation transitions from recently introduced grasses to dense tropical forest including both native and introduced species. In the region,

soils composed of rock or tephra mixed with organic matter are classified as Udiarents or Udifolists; soils with greater amounts of mineral fines relative to organic matter are classified as Hydrudands or Haplustands (Soil Survey Staff, 2015; Lincoln et al., 2014). Sampling locations were chosen in localities that showed little evidence of recent disturbance.

Soils were derived dominantly from a'a textured lava; however, some higher elevation sites (~600+ m) for the 2250 year flow were sampled on pahoehoe textured lava. The 500 year old soils form on a flow from Hualalai Volcano; all other soil samples came from flows derived from Mauna Loa. Hualalai and Mauna Loa flows differ chemically; Hualalai flows are alkalic whereas Mauna Loa are tholeiitic. Alkalic lavas tend to be more enriched in incompatible trace elements (Rb and Sr for example). Major element differences include increased Na and K in alkalic lavas versus increased Fe and Mg in tholeiitic lavas (Cohen et al., 1996; MacDonald and Katsura., 1964).

4.2 Soil analyses from Lincoln et al., (2014)

Soils were sieved to <2 mm and split into three parts and analyzed as follows. Soils were analyzed for total carbon and nitrogen and resin-extractable phosphorus (P) at Stanford University following NRCS Soil laboratory procedures (Soil Survey Staff, 1992). Soil samples were analyzed for major elements by lithium metaborate fusion and X-ray flourescence at ALS in Reno, NV. Additionally, cation exchange capacity and exchangeable cations were determined by leaching the soil with ammonium acetate buffered to pH 7 according to NRCS Soil laboratory methods at University of California, Santa Barbara (Soil Survey Staff, 1992). More detailed methods for these analyses are found in Lincoln et al. (2014).

4.3 Subsampling and Sr isotope analysis

Samples from the larger Kona dataset presented in Lincoln et al. 2014 were selected for Sr isotope analysis. Kona samples were chosen to cover all ages in the initial chronosequence (500, 1200, 2250, 4000 and 7500 years old) and were grouped into "dry", "medium" and "wet" precipitation ranges from the initial climosequence (950-1060 mm, 1180-1210 mm, and 1450-1500 mm respectfully). Base saturation data for only the selected samples can be found in Appendix A, Figure 1.

Isotope analyses were performed by inductively coupled plasma mass spectrometry on a Nu Plasma HR MC-ICP-MS at the ICPMS/TIMS Facility at Stanford University's School of Earth Sciences. Strontium isotopes for extractable Sr and residual Sr for each sample were determined. Extractable or plant accessible cations were extracted by leaching the soil with 1M ammonium acetate. Soil residue left over after extractable cations were removed (termed "residual" within the rest of the paper) was dissolved by microwave digestion using a CEM MarsXpress Microwave Digester in a solution of concentrated nitric, hydrofluoric and hydrochloric acids (5: 1.5: 1 ratio respectively). Strontium concentration for the extractable cations and residual soil was measured on a Nu Plasma HR-ICP-MS. Strontium for isotope analyses was isolated by column chemistry using SrSpec Resin. Machine mass fractionations were corrected using an exponential law, normalizing to $^{86}Sr/^{88}Sr = 0.1194$ and samples were corrected to the standard NBS-987 = 0.71026, as run by the Nu Plasma HR MC-ICP during the analysis. Internal error on the samples reported for two standard deviations was at most 0.00005.

4.4 Isotope mixing model and Sr fluxes

A simple isotope mixing model for two endmembers was applied to the extractable and residual Sr data. More complicated mixing models include concentrations of the isotope endmembers, however incorporation of these concentrations creates results independent of the actual Sr flux from the source. A more detailed look at the differences between the two mixing models can be found in Appendix B. Our model uses an atmospheric endmember (subscript a), either continental dust (residual data) or rainfall (extractable data), and a basalt endmember (subscript b) to calculate the percentage of Sr contributed by each endmember towards the sample to produce its isotopic signature (subscript s) (equation 1).

$$F_a = \frac{I_s - I_b}{a - I_b}, \quad F_b = 1 - F_a \tag{1}$$

Where, F is the proportion of Sr contributed by an endmember and I is the isotopic signature of the endmember or sample. While previous research provides ancillary evidence indicating some dust influence on the exchangeable Sr signature through weathering preference and possible rainfall derived Sr forcing on the residual soil Sr signature due to occluded pools of Sr in rainwater, we assume these influences are relatively small in order to provide a clear first description of incipient soil nutrient dynamics (Chadwick et al., 2009; Dauer and Perakis, 2014).

Approximate Sr flux rates applied over the ages of our study area and integrated to 30 cm soil depth were used to corroborate the results of the mixing model. Dust flux was approximated to be 1×10^{-5} g cm^{-2} yr^{-1} during interglacial times and a Sr concentration for the dust was estimated to be 200 ppm (Nakai et al., 1993; Rea, 1994). The dust derived Sr flux to the soil was 0.002 µg Sr cm^{-2} yr^{-1}. Assuming a rainfall concentration of ~1 ng g^{-1} of Sr and using the mean annual rainfall values, we estimate a rainfall derived Sr flux to the

soil of 0.10-0.15 ug Sr cm^{-2} yr^{-1}. It is likely not all of the exchangeable Sr introduced by rainwater interacts with mineral surfaces; Stewart et al. (2001) assumes that 15% of rainfall derived Sr sorbs onto soil exchange sites for soils on Kohala (Stewart et al., 2001). Counting only the Sr that makes it onto the exchange sites, we get a rainfall derived Sr flux to the soil of 0.0150 – 0.0225 ug Sr cm^{-2} yr^{-1}.

5. Results

Here I present data to first corroborate the connection between Sr and Ca in the soil exchange system. Next I show Sr concentration data to understand the patterns of Sr storage in the exchangeable and residual soil Sr pools and how this compares to Sr from the parent material. Finally, I present the Sr isotope data for both exchangeable and residual soil Sr and how patterns in Sr isotope values connect to lava flow age, precipitation and strontium concentration for both the residual and exchangeable soil Sr. All strontium concentration and isotope data are featured in Table 1.

Table 1. Soil sample names and site characteristics for those soils selected in this study for isotopic analysis from the larger young Kona chrono-climosequence originally set by Lincoln et al., 2014. Soil chemical data including extractable Sr, residual Sr and bulk soil Sr concentrations and ^{87}Sr/^{86}Sr values.

Sample Name	Sample MAP, mm	Sample Age, yr	Extract. Sr [ ], ppm	Extract. ^{87}Sr/^{86}Sr	Residual Sr [ ], ppm	Residual ^{87}Sr/^{86}Sr	Bulk Soil Sr [ ], ppm
LB 101	1200	500	5.022	0.7041680	12.828	0.7038633	17.850
LB 77	1200	500	3.386	0.7040885	12.618	no data	16.003
LB 75	1475	500	4.261	0.7041241	7.094	0.7037373	11.355
LB 97	1475	500	4.033	0.7042004	10.469	0.7038560	14.502
LB 106	1000	1200	0.218	0.7045791	13.774	0.7039106	13.992
LB 120	1030	1200	2.031	0.7048621	12.113	0.7040243	14.144
LB 133	1060	1200	1.034	0.7045254	11.231	0.7039552	12.265
LB 129	1180	1200	1.410	0.7045675	11.036	0.7039923	12.447
LB 70	950	2250	1.729	no data	8.846	0.7039008	10.576
LB 71	1000	2250	2.716	0.7056363	8.500	0.7045937	11.216
LB 57	1200	2250	2.413	0.7045239	3.841	0.7041437	6.254
LB 12	1450	2250	0.895	0.7064215	1.376	0.7071919	2.271
LB 31	1450	2250	0.963	0.7066526	1.401	0.7081093	2.363
LB 19	1500	2250	2.375	0.7046815	6.593	0.7042909	8.969
LB 34	1500	2250	2.462	0.7046450	6.425	0.7042850	8.887
LB 61	1000	4000	7.198	0.7055671	7.437	0.7054105	14.635
LB 63	1210	4000	4.154	0.7056169	3.514	0.7060522	7.667
LB 68	1420	4000	5.241	0.7045164	10.801	0.7043790	16.042
LB 38	950	7500	3.732	0.7057794	5.843	0.7049825	9.576
LB 81	975	7500	3.943	no data	10.820	0.7044786	14.764
LB 3	1000	7500	5.613	0.7056459	8.582	no data	14.195
LB 7	1200	7500	4.970	0.7055093	5.812	0.7060820	10.782
LB 47	1500	7500	0.273	0.7069779	1.000	0.7106612	1.273

5.1 Strontium and calcium concentration in the extractable fraction

The extractable Sr/Ca ratio (Figure 3) is relatively constant with increasing lava flow age, showing a similar response of Sr and Ca to soil development. There is however a spike in the ratio for two of the three 4000 year old soils, indicating some Ca loss where Sr is retained. Individual trends for extractable Ca and Sr concentration with flow age reveal more information on the increase in ratio for the 4000 year old soils and suggest potential patterns of soil leaching and rock weathering (Figure 4). Calcium concentration increases with age in the lowest precipitation grouping and decreases with age in the highest precipitation grouping. Strontium concentration follows similar patterns to Ca, however the 4000 year old lava flow has a high rainfall sample that shows an elevated Sr concentration where the Ca concentration is very low. Also notably, the extractable Sr and Ca for the 500 year old soils are elevated compared to the next two oldest soil age groups.
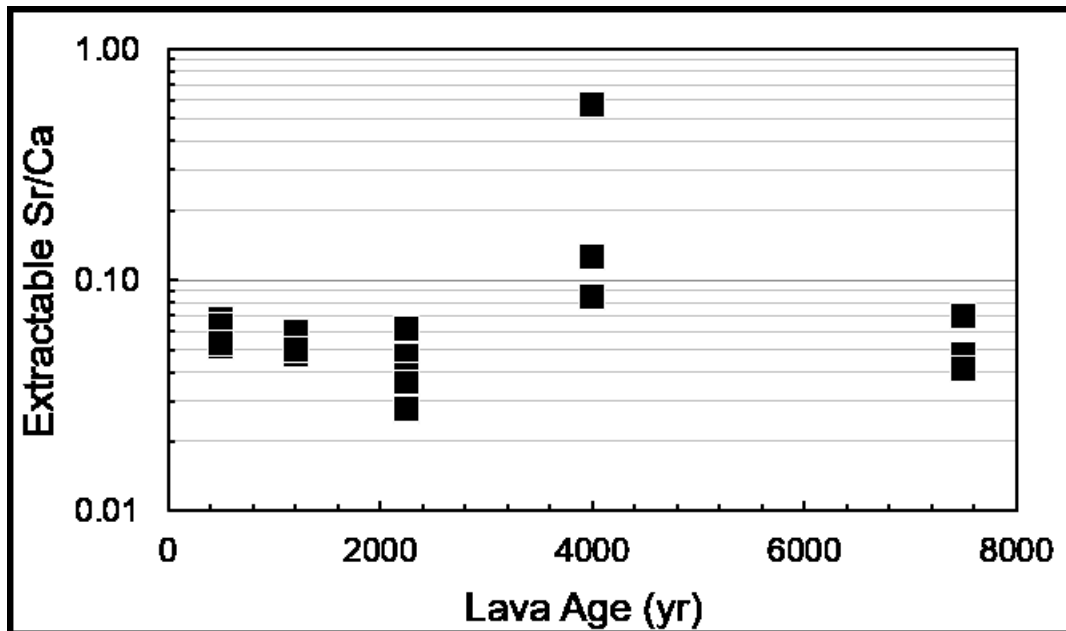

Figure 3. Ratio of extractable Sr to extractable Ca in soil compared to lava flow age. The 4000 year old soils show slightly elevated ratios compared to the other soils; which, show relatively constant Sr/Ca ratios with soil age.
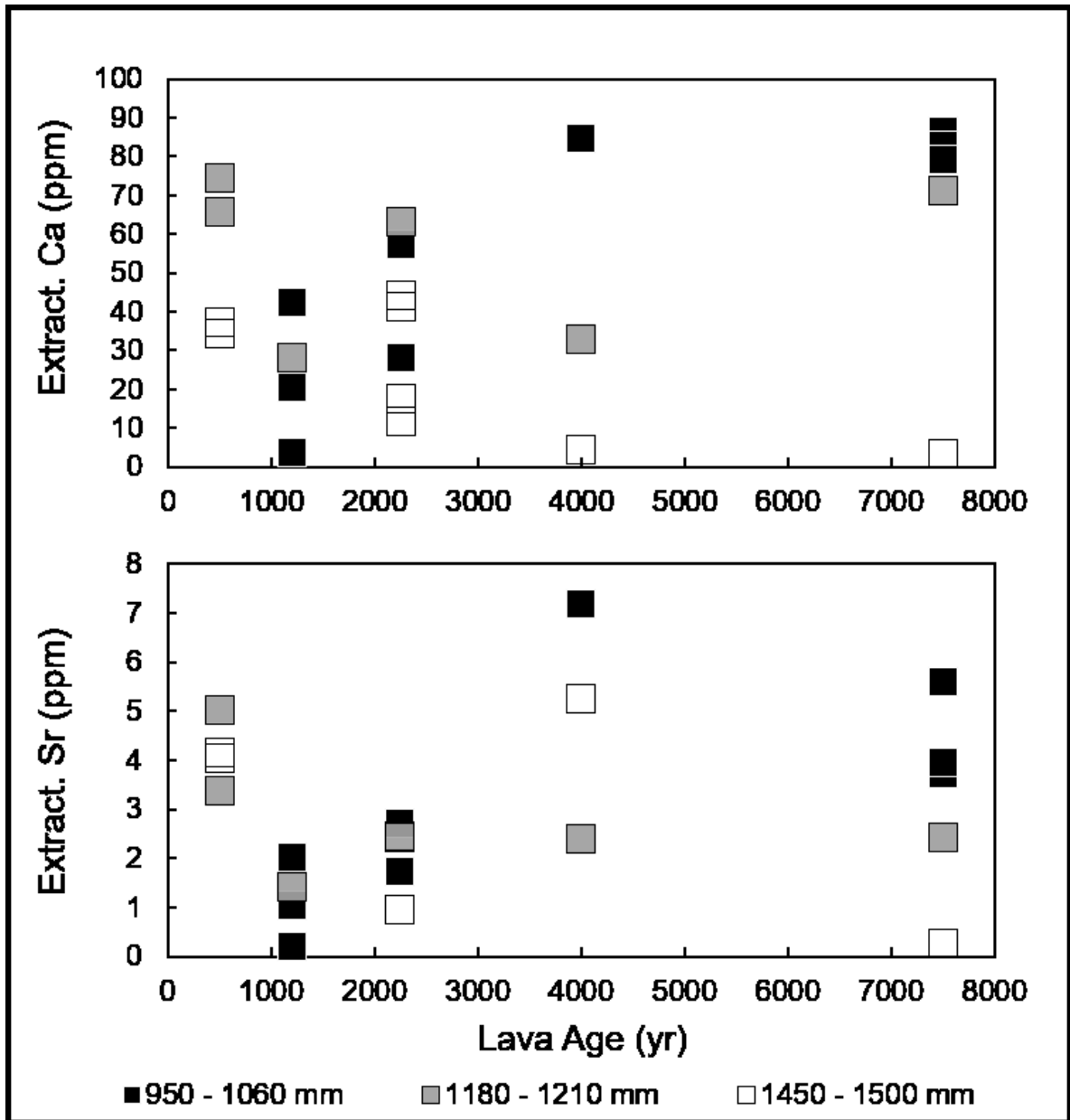
Figure 4. Extractable Ca and extractable Sr for the soil compared to lava flow age. Samples are denoted according to annual precipitation range. General trends with increasing soil age are in good agreement for Sr and Ca.

5.2 Strontium soil and parent material pools compared with age and climate

Relative changes among extractable Sr, residual and rock Sr were evaluated using

ratios of extractable Sr to residual Sr and bulk-soil Sr (extract. + resid. soil Sr) to rock Sr

(Fig 5). Excluding the 500 year old soils, the ratio of extractable Sr to residual-soil Sr

largely increases with soil age, with peaks in the ratio at the medium and dry sites of 4000

and 7500 year old soils (Figure 5a). Uniform extractable Sr loss is apparent in the wettest

precipitation grouping soils with ratio values between 0.2 and 0.6 for all soil ages (Figure

5d). The 500 year old soils have proportions of extractable Sr to bulk soil Sr on par with the

2250 year old soils (20-35%). Overall, bulk-soil Sr is a very small proportion (maximum of

7%) of Sr in the underlying rock (Figure 5b). Bulk-soil Sr is noticeably depleted in some of

the wet climate soils (2250 and 7500 soils), while other wet climate soils have some of the

highest proportions of bulk-soil Sr (500 and 4000 yr old soil). Dry-climate soils regardless

of soil age have relatively constant proportions of bulk soil Sr to rock Sr (Figure 5c). The Sr

values for parent material was determined using an average of five recent Mauna Loa

tholeiitic flows and nine fresh Haulalai alkalic flows (Table 2).

Sample Name	Flow Age (ka)	Source	Sr (ppm)
K5-05	2.2	mauna loa	303
K7-13	2.9	mauna loa	223
K5-28	5.7	mauna loa	322
K7-01	7.2	mauna loa	229
K7-07	7.8	mauna loa	290
[1266][13124][12353][13493][1494][15590]	fresh lava	haulalai	233
[1266][13124]	fresh lava	haulalai	150
[1266][13124][90]	fresh lava	haulalai	223
[9021][9016][13617]	fresh lava	haulalai	288
[9021][9016][13617]	fresh lava	haulalai	287
[9016][9021][13617]	fresh lava	haulalai	260
[9016][9021][13617]	fresh lava	haulalai	266
[9016][9021][13617]	fresh lava	haulalai	280
[9021][9016][13617]	fresh lava	haulalai	331
Average			263.214
Standard Deviation			± 46.265

Table 2. Strontium concentrations for rock samples used in figure 5. Samples represent relatively recent lava flows from both Hualalai and Mauna Loa. Haulalai samples are taken from Jackson et al., 2012 and Mauna Loa samples are from Cohen et al., 1996.
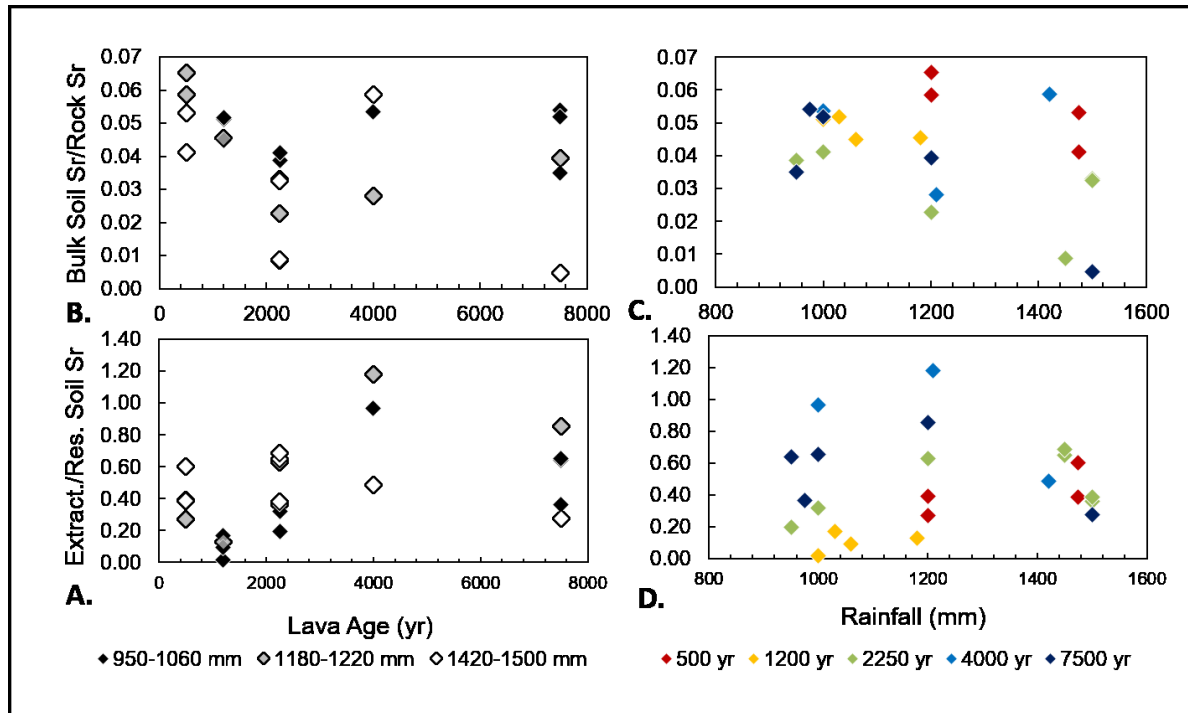
Figure 5. (a) Extractable soil Sr concentration: residual soil Sr concentration compared to lava flow age for Kona soil samples. (b) Bulk soil Sr concentration: rock Sr concentration compared to soil age for Kona soil samples. (c) Bulk soil Sr: rock Sr concentration compared to rainfall for the sampling sites in Kona. (d) Extractable soil Sr concentration: residual soil Sr concentration compared to rainfall for the sampling sites in Kona. Figures A and B are separated by average precipitation range (dry, medium and wet) and figures C and D are separated by underlying lava flow age (500, 1200, 2250, 4000 and 7500 years).

5.3 Strontium isotope trends with lava flow age, climate and Sr concentration

Strontium isotope data for extractable Sr and residual soil Sr are shown in Figure 6 as comparisons to sampling site mean annual precipitation and the lava flow age. As lava flow age increases, exchangeable $^{87}Sr/^{86}Sr$ initially increases and then plateaus at ~0.7057 (Figure 6b). Variability around this trend is contributed mainly by the wettest precipitation samples (Figure 6b). All precipitation groups exhibit distinct clustering of more radiogenic and less radiogenic extractable $^{87}Sr/^{86}Sr$ values (Figure 6c). Residual soil $^{87}Sr/^{86}Sr$ values tend to follow the exchangeable Sr isotope patterns with lava flow age and precipitation (Figures 6a, d). Notably, a few samples in the wettest precipitation grouping have much higher $^{87}Sr/^{86}Sr$ values than the comparable extractable Sr counterparts; one sample plots

19

near the continental dust endmember with a Sr isotopic value of 0.7106 (Figure 6a). High and low $^{87}Sr/^{86}Sr$ groupings for the residual soil only become obvious at higher precipitation amounts, and the separation between isotope groupings increases with increasing rainfall (Figure 6d).

Strontium isotopes, and their respective Sr concentrations, provide further insight into the different processes controlling base cation trends with soil age and precipitation. The extractable Sr isotope values exhibit different trends among the dry, wet and intermediate rainfall groups when compared to Sr concentration (Figure 7). The highest precipitation group shows a distinct decrease in the $^{87}Sr/^{86}Sr$ values towards the basalt endmember with increasing Sr concentration. Strontium isotopes shift from 0.7065 at 0-1 ppm Sr to 0.7045 with Sr concentrations >2 ppm. In contrast, the $^{87}Sr/^{86}Sr$ ratios of the 950-1060 mm/yr rainfall group increase with increasing Sr concentration. Strontium isotope values for low Sr concentrations are 0.7045, but they rise to 0.7055 above 2 ppm. The medium precipitation group has variable Sr isotope values which span the range defined by the dry and wet sample groups. Connecting Sr concentrations to the distinct trends between extractable Sr isotopic data and lava flow age/precipitation (Figures 6b, c) links these soil forming factors to soil base cation status. In general, as the soils increase in age so does the extractable Sr concentration and the extractable Sr isotope values. The wettest precipitation group shows the greatest deviation from this pattern by showing an inverse trend between concentration and isotope value that is age independent.

In contrast to the extractable Sr, residual Sr concentration is always negatively associated to residual Sr isotopes. All residual Sr isotopes decrease to the rock end-member with increasing Sr concentration (Figure 8). The $^{87}Sr/^{86}Sr$ ratio drops from over 0.7100 at ~1

ppm to 0.7035 at 15 ppm Sr. Adding in residual Sr concentration data to Figures 6a, d links

the residual soil Sr pool dynamics to soil forming factors. Residual Sr isotopes and

concentrations mirror the patterns of the wettest climate group for extractable Sr: high

concentrations of residual Sr match with low $^{87}Sr/^{86}Sr$ isotope signatures and vice versa with

correlation to lava flow age. The difference in $^{87}Sr/^{86}Sr$ values and between the clustering of

high Sr isotopes/low concentrations and low Sr isotopes/high concentrations per climate

group grows with increasing precipitation (Figure 6d). When compared to Sr concentration,

distinct trends in $^{87}Sr/^{86}Sr$ ratios between climate groups are apparent for extractable Sr,

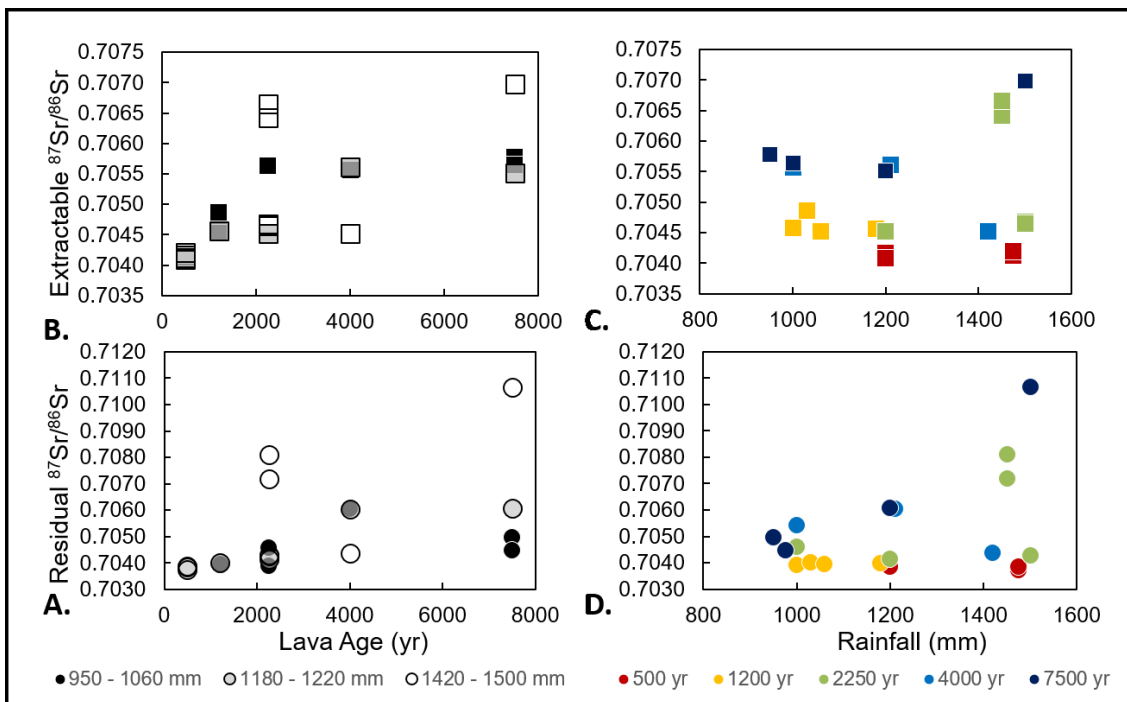while residual Sr isotopic data behave similarly regardless of climate group.

Figure 6. (a) Residual soil Sr $^{87}Sr/^{86}Sr$ compared to lava flow age for the selected Kona chrono-climosequence samples. (b) Extractable Sr $^{87}Sr/^{86}Sr$ compared to lava flow age for the selected samples in the Kona chrono-climosequence. (c) Residual soil Sr $^{87}Sr/^{86}Sr$ compared to mean annual rainfall for selected samples in the Kona chrono-climosequence. (d) Extractable Sr $^{87}/Sr^{86}$ compared to mean annual rainfall for selected samples in the Kona chrono-climosequence. Figures A and B are separated by rainfall range (dry, medium and wet) and figures C and D are separated by underlying lava flow age (500, 1200, 2250, 4000 and 7500 years).
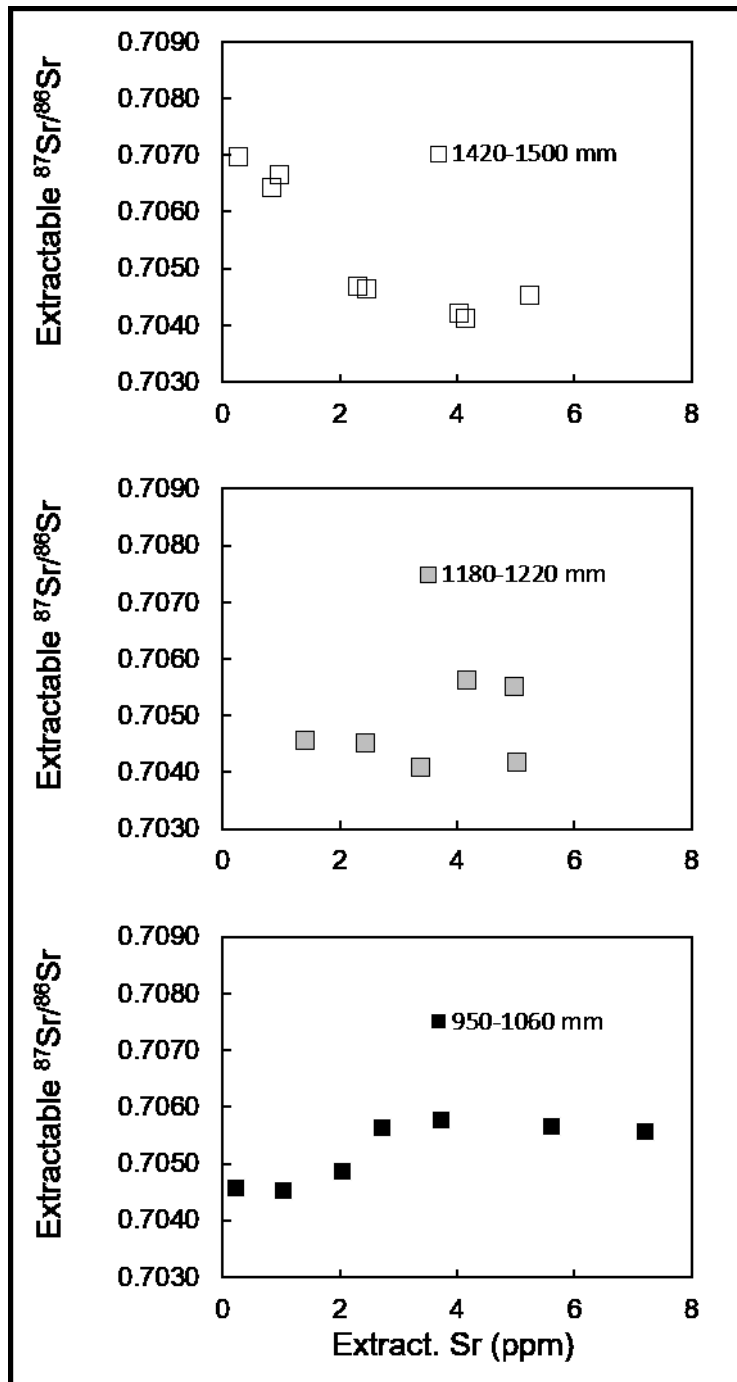
Figure 7. Extractable Sr isotope values compared to extractable Sr concentrations, separated by average annual precipitation range. Sr isotope values decrease with increasing Sr concentration in the wettest soils, which contrasts with the pattern for the driest soils. The medium precipitation soils span both the wet and dry soil trends.
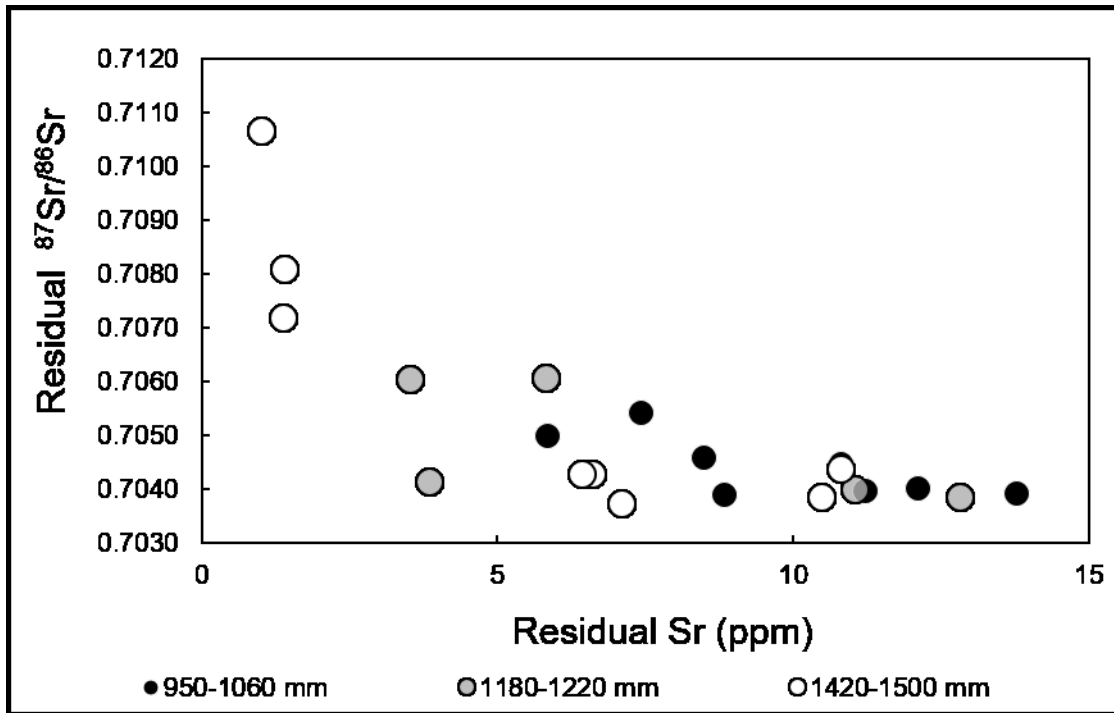
22

Figure 8. Residual soil Sr isotope values compared to residual soil Sr concentrations, separated by average annual precipitation range. All Sr isotope values decrease with increasing Sr concentration.

6. Discussion

6.1 Processes controlling extractable Sr isotopes

Soils from the lowest rainfall range show a clear increase followed by a plateau in $^{87}Sr/^{86}Sr$ values with increasing soil age, which is mirrored in Sr concentration. Strontium isotopic values of 0.7055 for concentrations greater than 2 ppm suggests that both rainfall and rock weathering are independently contributing base cations to the soil. At lower rainfall levels, soils experience a severely diminished leaching intensity, allowing rainfall to add cations to soil instead of strip them away. With increasing soil age, there is an increase in Sr and other base cations sourced from both rainfall and rock weathering (Figures 4, 5). The addition of Sr to the soil by rainfall produces the observed increase in extractable Sr compared to residual Sr over time (Figure 4a). Rock weathering does contribute some

23

cations to the extractable pool over time, preventing the $^{87}Sr/^{86}Sr$ values from consistently increasing towards the rainfall endmember (0.7092). However, the relative age of these soils coupled with the low rock-weathering rates, inhibits complete depletion of the rock-derived Sr pool. Ratios of total soil Sr to rock Sr ratios rarely exceed 7% (Figure 5b). The small proportion of rock-derived cations contributed to the soil enables the dilute but constant source of cations added by rainfall to shift the Sr isotopic signature to higher values. Assuming only 15% of the total rainfall-derived Sr is retained on labile sites, 2 – 4 ppm of exchangeable Sr is still delivered to the exchangeable pool over 4000-7500 years based on time-integrated rainfall derived Sr flux calculations (Figure 9). Over time the buildup of rainfall-derived cations manifests in an elevated isotopic signature and an increased exchangeable Sr concentrations.

At higher rainfall levels, the base saturation data from Lincoln et al. (2014) (Figure 2) suggests two different processes at work: increased rock weathering and increased soil leaching. Regardless of the soil age, extractable strontium isotopes from the wettest precipitation group depict the balance between leaching increases and rock weathering rate increases (Figures 6b, 7). Lower extractable Sr concentrations are associated with $^{87}Sr/^{86}Sr$ values closer to the rainfall end member, whereas higher concentrations of extractable Sr match more rock-derived Sr isotope signatures. This isotope and concentration pattern is in contrast to the age dependent, driest sample group where higher concentrations of extractable $^{87}Sr/^{86}Sr$ match more rainfall-derived Sr signatures.

A simple mixing model describes the contributions of extractable Sr from rainfall and basalt (Figure 10). For the wettest rainfall range, rainfall derived Sr makes up 40-60 % of the Sr on the soil exchange in the sites with the lowest Sr concentrations. In contrast, sites

in the same precipitation range but with higher Sr concentrations, have ~80% of the

extractable Sr provided by the rock. Independent calculations of time-integrated rainfall-

derived Sr flux demonstrates that more than enough (>2x) extractable Sr derived from

rainfall is available to fill the exchange sites in the areas most depleted of Sr (Figure 9).

Likely, less than the assumed 15% rainfall- derived Sr is interacting with soil exchange sites

due to fast hydrologic flow through void spaces among the lava clinkers in these incipient

soils (Stewart et al., 2001). The flux of rainfall-derived Sr is small compared to the Sr flux

supplied by rock weathering in older, more developed soils (Stewart et al., 2001, Chadwick

et al., 2009). Thus as weathering limitation is overcome at some of these higher precipitation

sites, soil exchange sites are predominantly filled by rock-derived Sr regardless of the
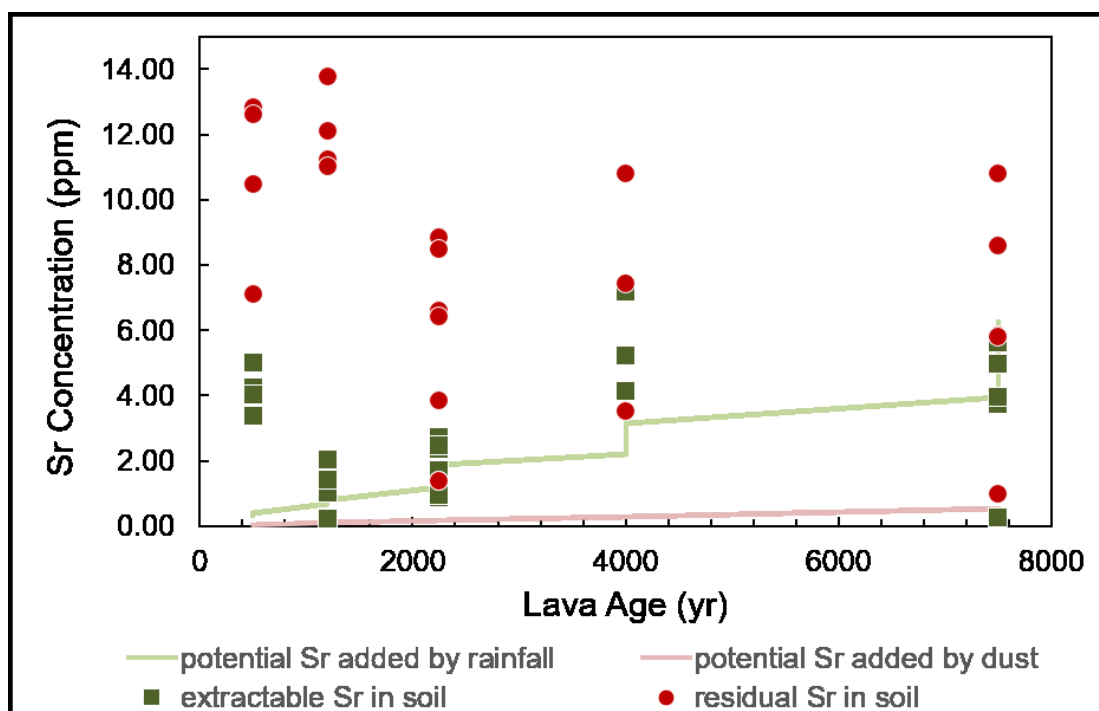
rainfall-derived Sr flux.

Figure 9. Cumulative potential Sr added by atmospheric inputs plotted against lava flow age.
Actual extractable Sr and residual soil Sr concentrations are overlaid. Rainfall Sr input varies by
mean annual precipitation, Sr input via dust deposition does not vary by rainfall amount.
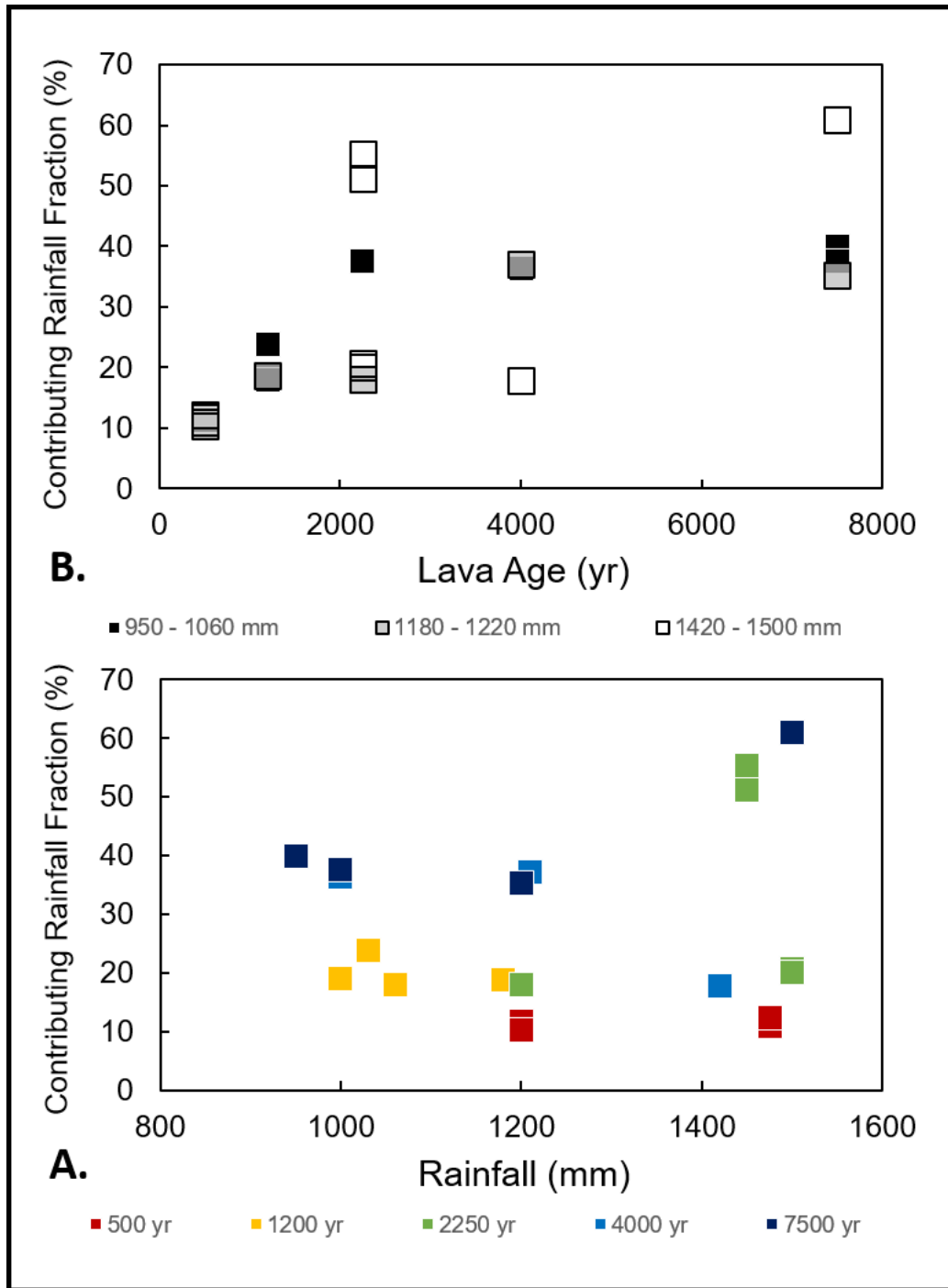
Figure 10. Mixing model results for Sr isotopes of the extractable Sr. (a) Fraction of extractable Sr contributed by rainfall with respect to mean annual rainfall. Samples are denoted by lava flow age. (b) Fraction of extractable Sr contributed by rainfall with respect to lava flow age. Samples are separated by mean annual precipitation grouping.

6.2 Variability

Incipient soil formation in tropical volcanic landscapes is strongly influenced by lava flow variability (Soil Survey Staff, 2015). Uneven lava flows and discontinuous cracking during cooling creates an irregular depositional surface for the locally derived organic material, ash, and tephra that provide fines to fill the larger void spaces in the lavas. There is an inherent patchiness in the water retention of these recent soils which feeds strong variability in the local soil forming environment. All of these factors create differences in the degree of soil development possible for samples sites on the same age flows and in the same climate. In addition to in situ factors, atmospheric influences can also contribute to soil development variability.

6.2.1 The 500 year old soil anomaly

Although the data generally show increasing base saturation with soil age the youngest soils have higher base saturation than expected based on observations from older soils. I suggest that this result provides an example of soil heterogeneity caused by environmental factors. In this case localized ash and tephra fall from Hualalai appear to be controlling the nutrient status of the 500 year old soils. The tight grouping of extractable Sr isotope values near the bedrock end member suggests a dominance of volcanically sourced base cations in the soil (Figure 6b). The higher surface area of the added Hualalai ash increases weathering surface area and lowers the kinetic limitation to parent material weathering rates as compared to those for lava rock. Higher base saturations can be expected for the young age of the soils due to faster rock weathering rates (Lincoln et al., 2014). The isotope mixing model results corroborate the contributions of rock derived Sr, ~90% of the Sr in the extractable pool is supplied by the rock (Figure 10).

27

6.2.2 Differences in leaching intensity at the wettest soil sites

Mapping Sr isotopes to their sampling site elevations provides a metric for understanding how isotopic composition varies with distance to ocean and also precipitation style and quantity. The clustering of Sr isotope values into two groups within the wettest precipitation range seems to be due to variation in rainfall style within this higher rainfall area, which alters the leaching intensity these soils experience. Strontium isotopic values show variability but no specific trend for elevations below 600 m and above 800 m (Figure 11). However at 600 m elevation both residual and extractable Sr isotope values increase, reaching values of 0.7065 for extractable Sr and 0.7106 for residual Sr. Above 800 m, both extractable and residual Sr isotopes are relatively low and less varied than the group below 600 m. Samples taken at the maximum lifting condensation level (LCL, elevation 600 m for Kona), could experience more intense, but sporadic rain events because the LCL reaches this elevation when the air surface temperatures across the region are also peaking during the typical daily cycle. Thus, a higher energy environment is produced for the potential rainfall events expected to begin with temperatures in the region cooling after the daily maximum (Yang and Chen, 2003; Giambelluca et al., 2013). The LCL rarely pushes above 600 m elevation, thus samples from elevations >600 m experience a persistently moist environment from the sustained cloud bank. The 600 m elevation corresponds roughly to the maximum elevation of cloud bank formation and increased intense precipitation zone (Yang and Chen, 2003; Giambelluca et al., 2013). If rock weathering rates do not scale with the increased leaching by higher intensity rainfall events, soil Sr is lost and only partially replaced by the Sr input by rainfall (Figures 7, 11).

In contrast, soils subject to more prolonged light rain (soils found at elevations above

600 m) may actually experience elevated rock weathering, transitioning to mineral soil

dominant as evidenced from their taxonomic classification (Udarents compared to

Udifolists). Accounting for the shorter timescales of soil development and still some kinetic

limitation to rock weathering along this transect, the rock retains a large proportion of its

original cation pool (Figure 5b) despite isotope values indicating rock weathering

contributing 80-90% of extractable Sr in the wet sites not experiencing intense leaching
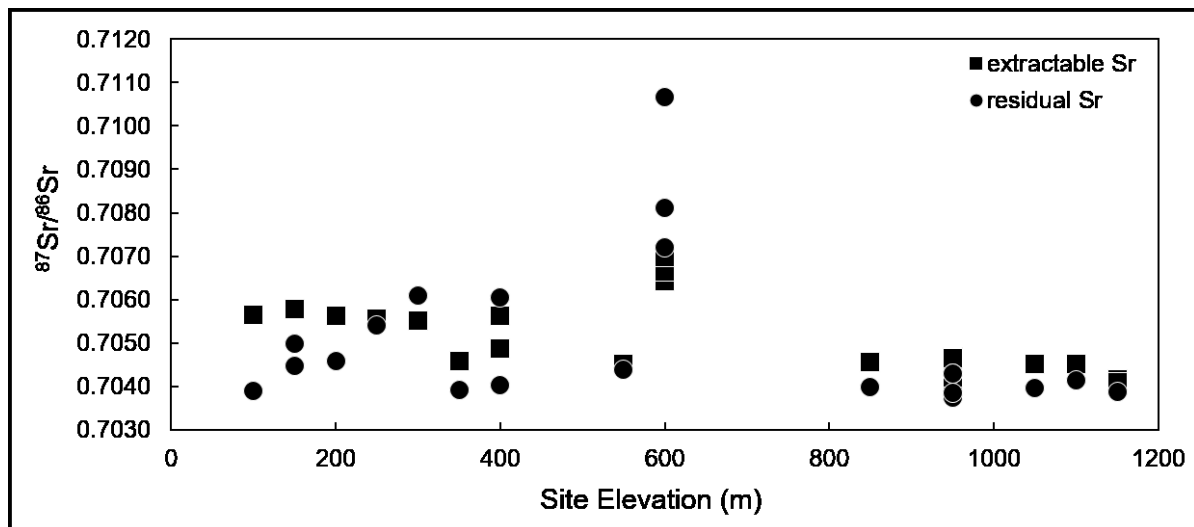
events (Figure 10).

Figure 11. Residual and extractable Sr isotopes for soil compared to sample site elevation. The noticeable spike in isotope values at 600 m elevation corresponds with increased cloud cover and rainfall at the same elevation. Soils at the 600m elevation are 2250 and 7500 years old.

6.3 Process thresholds and dust accumulation

The soils in the intermediate precipitation group show extractable Sr isotopic values

that are divided between the wet and dry soil trends suggesting a process shift at ~1200 mm

of rain annually. Above 1200 mm of rain, a more positive water balance drives increased

rock weathering and soil leaching, allowing the intensity of rainfall events to control the rate

and style of soil development. Below 1200 mm of rain, negative water balance minimizes

29

both weathering and leaching producing a condition where cations are contributed to the extractable pools by both sources, increasing the extractable Sr concentration with soil age. Low rock weathering rates in the drier climate impart only a small proportion of the total rock Sr to the extractable pool, which in turn allows the dilute concentration of rainfall-derived Sr to be expressed in the extractable Sr isotopic signature.

I expect a prevalence of kinetic limitation to rock weathering due to rapid water flux through large pore spaces and low reactive surface areas of fresh lavas (White and Brantley, 2003; Maher, 2010). Despite enhanced conversion of residual Sr to extractable Sr at higher rainfalls, limited rock weathering rates play a role in the residual Sr dynamics (Stewart et al., 1998). Depletion in both the residual soil and extractable Sr pools, as observed in several soils from the wettest climate grouping (Figures 7, 8) can occur when rock weathering is unable to replenish leaching losses of Sr from the extractable and residual pools. The low concentrations of Sr in these pools enhance the influence of small amounts of Sr contributed from continental dust; $^{87}Sr/^{86}Sr$ residual values > 0.7035 (Figure 8). Multiple samples from a 10,000 year old transect also in the Kona region show elevated Sr isotopic signatures for the bulk soil indicating measureable dust contributions from continental sources (Chadwick et al., 2009). When rock-derived Sr is in low enough proportions, the accumulation of dust is observable in the residual soil Sr isotopic signature. While only one soil shows a nearly pure dust influenced signature, the slow buildup of exogenous dust in the residual soil is observable for the lower concentrations of residual Sr in the soil (Figures 10, 12).

The mixing model reveals increasing contributions of dust (2% to ~50% dust-derived Sr) to the residual soil Sr pool with decreasing concentration of residual Sr and increasing Sr isotope signatures (Figure 12). Time-integrated dust-derived Sr flux calculations corroborate

the mixing model results, producing dust-derived Sr fractions within 15% of the mixing model results, but almost always underestimating the dust-derived fraction. Dust flux calculations only slightly underestimate the mixing model dust derived Sr fractions. Likely the underestimation by these flux calculations could be attributed to the exclusion of any occluded rainfall-derived Sr in a mixing model. Neodynium isotopes and rare earth element anomalies would allow me to refine the sources of dust in these incipient soils.
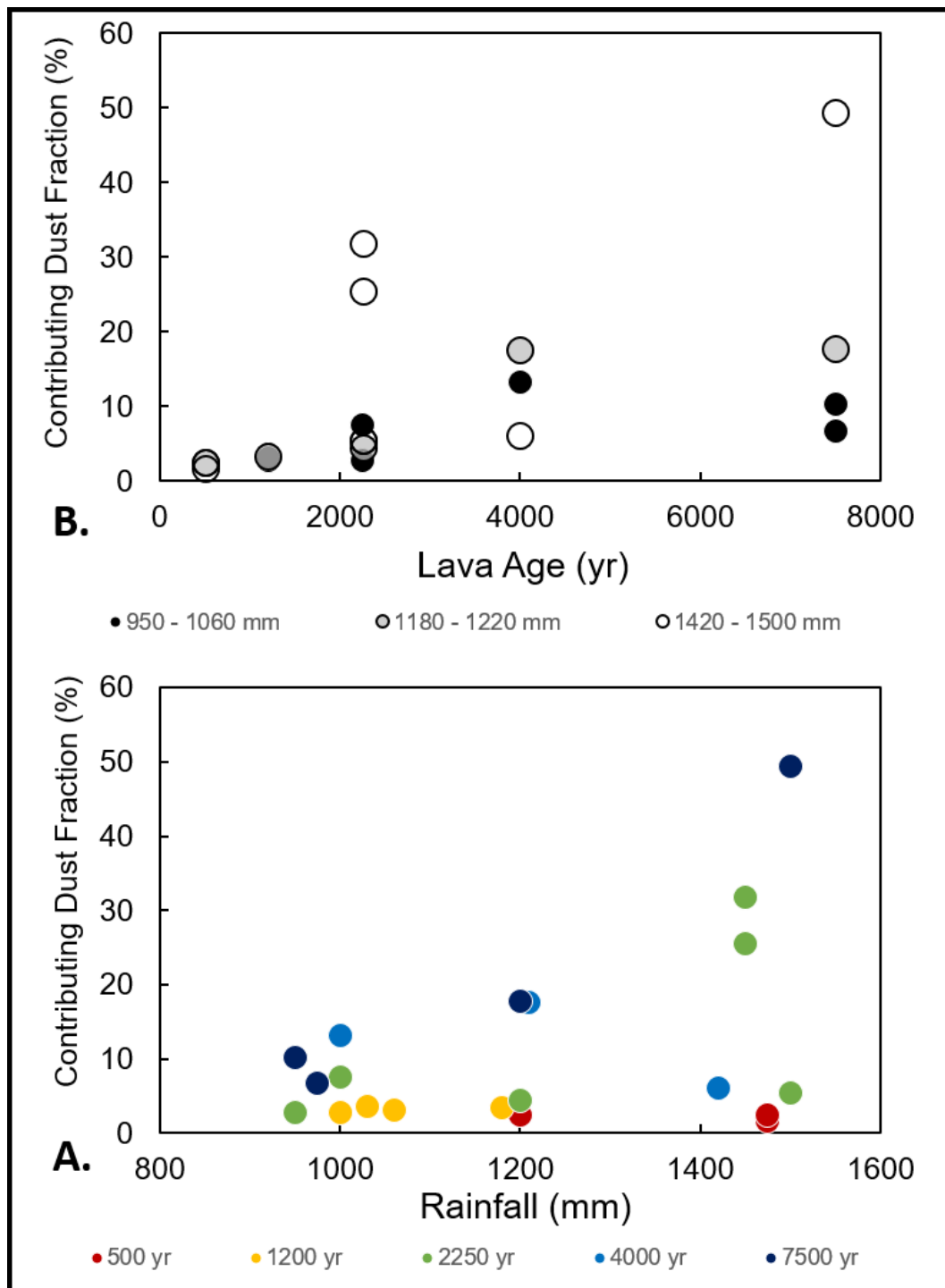
Figure 12. Mixing model results for Sr isotopes of the residual soil Sr. (a) Fraction of residual Sr contributed by dust deposition with respect to mean annual rainfall. Samples are denoted by lava flow age. (b) Fraction of residual Sr contributed by dust deposition with respect to lava flow age. Samples are separated by mean annual precipitation grouping.

7. Conclusion

Kinetic constraint of parent material weathering during incipient soil development leaves room for exogenous sources of base cations to play important roles in soil nutrient budgets. In landscapes where both weathering- and rainfall-derived base cation contributions to soil exchange surfaces are low, nutrient availability may be limited. In Kona, kinetic constraint to rock weathering is implied by the low proportion of bulk Sr compared to that of its rock substrate. Since there are low concentrations of bulk-soil Sr derived from rock weathering, the contribution of dilute atmospheric Sr fluxes becomes much more important. Precipitation is a driving factor controlling the proportion of atmospheric influence. Soils in drier climates experience dramatically reduced leaching intensities, leading to a buildup of rainfall-derived extractable Sr in the soil over time. Rainfall-derived Sr, in addition to the small extractable Sr input from rock weathering, produces more radiogenic extractable Sr isotope values over time. Extractable Sr concentrations and isotope signatures increase gradually with increasing lava flow age for soils in drier climates. Rock weathering is known to increase with higher rainfall amounts, however varied rainfall patterns within the highest precipitation sampling group create a range in the soil leaching intensities as well. Soils see a decline in concentration of base cations supplied by basalt and a dilute resupply by rainfall in areas where leaching intensity is increased, while soils in weathering conducive (lower leaching intensity, but still high rainfall) environments show higher base saturations and Sr signatures closer to the rock endmember. Soils in medium precipitation climate ranges, ~1200 mm/yr, show extractable Sr isotope signatures that fit within the wet and dry trends; indicating the critical precipitation amount that marks a shift between these two processes occurs around 1200 mm/yr in the Kona region. Residual soil Sr is susceptible

to leaching losses after it is released by weathering, thus several of the wettest precipitation group soils exhibit both residual and extractable Sr loss. In these soils dust accumulation is very apparent as reflected in the Sr isotope signature. Dust is detectable, though often in very small proportions, in the Sr signature for all residual soils because of the low bulk soil Sr concentrations.

References

Amundson R., Heimsath A., Owen J., Yoo K., Dietrich W.E., 2015. *Hillslope soils and vegetation*. Geomorphology, v. 234, p. 122-32.

Brantley S.L., Bandstra J., Moore J., White A.F., 2008. *Modelling chemical depletion profiles in regolith*. Geoderma, v. 145, p. 494–504.

Capo R.C., Stewart B.W., Chadwick O.A., 1998. *Strontium isotopes as tracers of earth surface processes: theory and methods.* Geoderma, v. 82, p. 197–225.

Chadwick O.A., Derry L.A., Vitousek P.M., Huebert B.J., Hedin L.O., 1999. *Changing sources of nutrients during four million years of ecosystem development.* Nature, v. 397, p. 491–97.

Chadwick O.A., Gavenda R.T., Kelly E.F., Ziegler D., Olson C.G., Elliott W.C., Hendricks D.M., 2003. *The impact of climate on the biogeochemical functioning of volcanic soils.* Chemical Geology, v. 202, p. 193–221.

Chadwick O.A., Derry L.A., Bern C.R., Vitousek P.M., 2009. *Changing sources of strontium to soils and ecosystems across the Hawaiian Islands*. Chemical Geology, v. 267, p. 64-76.

Clow D.W., Drever J.I., 1996. *Weathering rates as a function of flow through an alpine soil.* Chemical Geology, v. 132, p. 131–41.

Cohen A.S., O'Nions R.K., Kurz M.D., 1996. *Chemical and isotopic variations in Mauna Loa tholeiites.* Earth and Planetary Science Letters, v. 143, p. 111-24.

Dauer, J.M., Perakis, S.S., 2014. *Calcium oxalate contribution to calcium cycling in forests of contrasting nutrient status.* Forest Ecology and Management, v. 334, p. 64-73.

Dixon J.L., Riebe C.S., 2014. *Tracing and pacing soil across slopes*. Elements, v. 10, p. 363-68.

Gabet E.J., Mudd S.M., Milodowski D.T., Yoo K., Hurst M.D., Dosseto A., 2015. *Local topography and erosion rate control regolith thickness along a ridgeline in the Sierra Nevada, California*. Earth Surface processes and Landforms, v. 40, p. 1779-90.

Giambelluca T.W., Nullet M.A., Schroeder T.A., 1986. *Rainfall atlas of Hawaii.* State of Hawaii Department of Land and Natural Resources Report R76, Honolulu.

Giambelluca T.W., Chen Q., Frazier A.G., Price J.P., Chen Y.-L., Chu P.-S., Eischeid J.K., Delparte D.M., 2013. *Online rainfall atlas of Hawai'i.* Bull. Amer. Meteor. Soc. v. 94, p. 313-16.

Heimsath A.J., 2012. *Quantifying processes governing soil-mantled hillslope evolution, Hydropedology.* Elsevier, chpt. 7, p. 205-42.

Hofmann A.W., 1997. *Mantle geochemistry: the message from oceanic volcanism.* Nature, v. 285, p. 219-29.

Jackson M.G., Weis D., Huang S., 2012. *Major element variations in Hawaiian shield lavas: Source features and perspectives from global ocean island basalt (OIB) systematics.* Geochemistry, Geophysics, Geosystems, v. 13, p. 1-24.

Jenny H., 1941. *Factors of Soil Formation: A system of Quantitative Pedology.* Dover Publications, Inc.

Jenny H., 1973. *The Pygmy forest ecological staircase: description and interpretation.* University of California.

Kennedy M.J., Chadwick O.A., Vitousek P.M., Derry L.A., and Hendricks D.M., 1998. *Changing sources of base cations during ecosystem development, Hawaiian Islands.* Geology, v. 26, p. 1015–18.

Kurtz A.C., Derry L.A., Chadwick O.A., 2001. *Accretion of Asian dust to Hawaiian soils.* Geochim Cosmochim Acta, v. 65, p. 1971–83.

Ladefoged T.N., Kirch P.V., Gon S.O.III, Chadwick O.A., Hartshorn A.S., Vitousek P.M., 2009. *Opportunities and constraints for intensive agriculture in the Hawaiian archipelago prior to European contact.* J Archaeol Sci, v. 36, p. 2374–83.

Leopold L.B., 1949. *The interaction of trade wind and sea breeze, Hawaii.* J of Meteorology, v. 6, p. 312-20.

Lincoln, N., Chadwick, O.A., Vitousek, P.M., 2014. *Indicators of soil fertility and opportunities for precontact agriculture in Kona, Hawai'i.* Ecosphere, v. 5, p. 1-15.

MacDonald G.A., Katsura T., 1964. *Chemical composition of Hawaiian lavas.* J of Petrology, v. 5, p. 82-133.

Maher K., Steefel C.I., White A.F., Stonestrom D.A., 2009. *The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California.* Geochimica et Cosmochimica Acta, v. 73, p. 2804–31.

Maher K., 2010. *The dependence of chemical weathering rates on fluid residence time.* Earth and Planetary Science Letters, v. 294, p. 101-10.

Monastersky, R., 2015. *The human age.* Nature, v. 519, p. 144-47.

Nakai S., Halliday A.N., Rea D.K., 1993. *Provenance of dust in the Pacific Ocean.* Earth and Planetary Science Letters, v. 119, p. 143–57.

Soil Survey Laboratory Staff, 1992. *Soil survey laboratory methods manual.* Soil Survey Investigations, Report Number 42, Volume 2.0.

Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture. Web Soil Survey. Available online at http://websoilsurvey.nrcs.usda.gov/. Accessed [September/1/2015].

Porder S., Hilley G.E., Chadwick O.A., 2007. *Chemical weathering, mass loss, and dust input across a climate by time matrix in the Hawaiian Islands.* Earth and Planetary Science Letters, v. 258, p. 414–27.

Stewart B.W., Capo R.C., Chadwick O.A., 1998. *Quantitative strontium isotope models for weathering, pedogenesis and biogeochemical cycling.* Geoderma, v. 82, p. 173-95.

Stewart B.W., Capo R.C., Chadwick O.A., 2001. *Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils.* Geochim Cosmochim Acta, v. 65, p. 1087-99.

Vitousek P.M., Kennedy M.J., Derry L.A., Chadwick O.A., 1999. *Weathering versus atmospheric sources of strontium in ecosystems on young volcanic soils.* Oecologia, v. 121, p. 255–59.

Vitousek P.M., 2004. *Nutrient cycling and limitation: Hawai'i as a model system.* Princeton University Press.

Vitousek P.M., Ladefoged T.N., Kirch P.V., Hartshorn A.S., Graves M.W., Hotchkiss S.C., Chadwick O.A., 2004. *Soils, agriculture, and society in precontact Hawai'i*. Science, v. 304, p. 1665–68.

Vitousek P.M., Chadwick O.A., 2013. *Pedogenic thresholds and soil process domains in basalt-derived soils.* Ecosystems, v. 16, p. 1379-95.

White A.F., Brantley S.L., 2003. *The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field?.* Chemical Geology, v. 202, p. 479–506.

White A.F., Blum A.E., Schulz M.S., Vivit D.V., Stonestrom D.A., Larsen M., Murphy S.F., Eberl D., 1998. *Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: I. Long-term versus short-term weathering fluxes.* Geochim Cosmochim Acta, v. 62, p. 209–26.

Yang Y., Chen Y.-L., 2003. *Circulations and Rainfall on the Lee Side of the Island of Hawaii during HaRP*.* Monthly Weather Review, v. 131, p. 2525–42.

Appendix A. Base saturation data for the selected soil samples

Samples selection for this study was targeted at understanding climate and lava flow age influence on base cation dynamics during incipient soil formation. Careful consultation on the original sampling campaign by Lincoln et al., 2014 helped determine which samples should be selected to achieve our research goals.
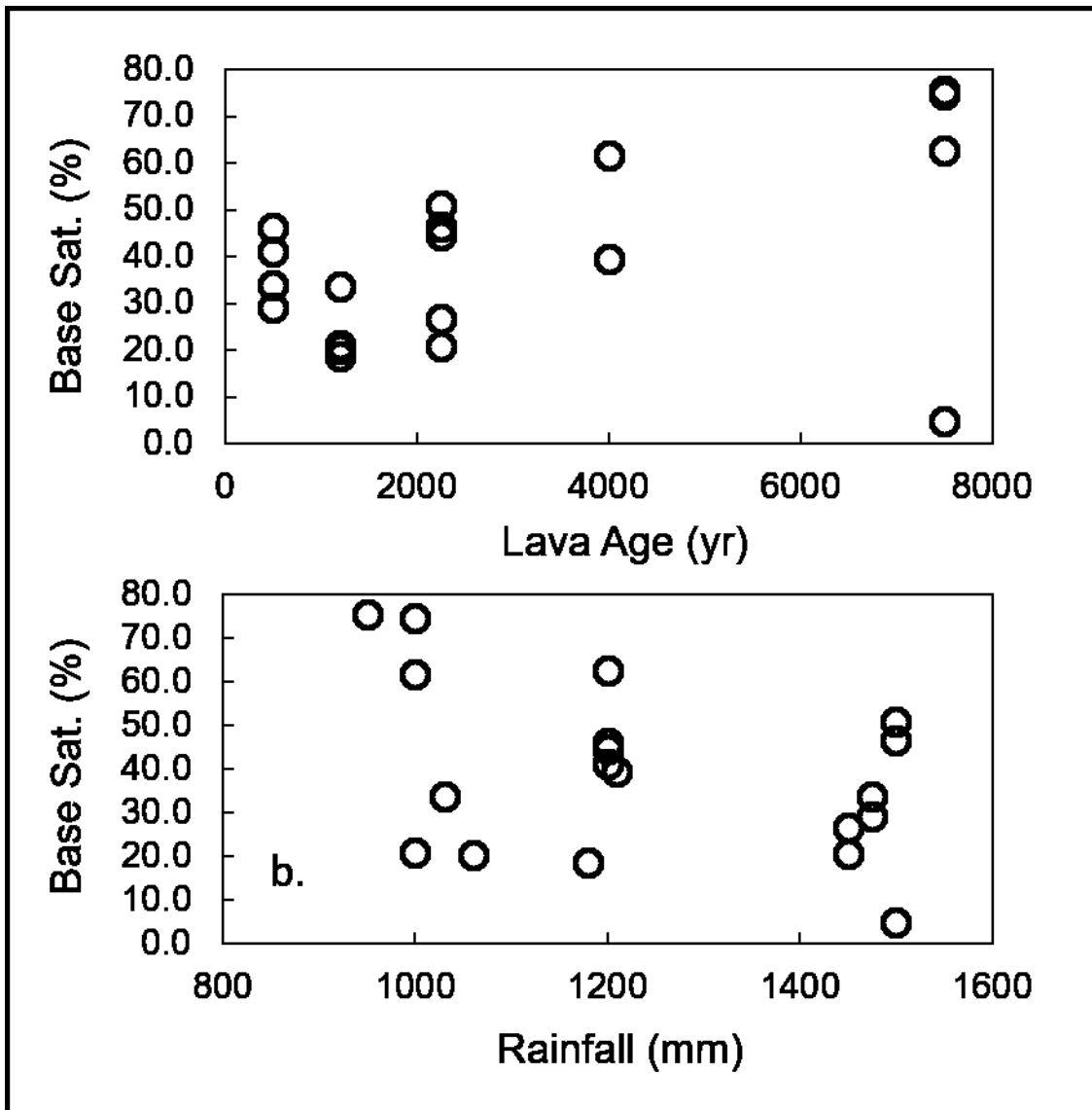
Appendix 1, Figure 1. Base saturation for the Kona compared to the lava flow age (a) and the annual rainfall (b). The rainfall range for each age group is 960-1500, with the exception of the 500 year old soils which are missing a "dry" sample and the 1200 year old group which is missing samples in the "wet" precipitation range.

Appendix B. Mixing model discussion

Mixing models to determine proportions of each endmember contributing to an isotope signal in a sample can include the concentration of an endmember or not. Inclusion of concentration imparts a dependence on the size of the Sr pool in each endmember, such that the influence on the isotopic signature is based on how much of a pool is needed to produce the isotopic value and the difference between pools. Using mixing between rock derived Sr and rainfall derived Sr as an example: the concentration of Sr in rainwater is very small compared to the concentration of Sr in the rock, therefore when using a concentration and isotope value mixing model, any increase in the $^{87}Sr/^{86}Sr$ value of a sample from the rock endmember isotope value (0.7035) produces rainfall contribution proportions of ~99% or more (Appendix b, Figure 1a). The results imply that you would need monumentally more rainwater than rock to produce a sample whose isotopic signature is not identical to the rock Sr signature of the Sr in the sample. Mixing models which exclude concentration allow a sample's isotope value to be influenced by the flux of Sr from each pool, not just the total quantity of Sr in each pool. Kinetic limitation to rock weathering can lower the flux of Sr to the soil exchange such that fluxes of Sr to the soil exchange complex by rainfall are in similar enough magnitudes to influence the Sr isotope signature of the exchangeable Sr, despite the large differences in the Sr concentration of each endmember (Appendix b, Figure 1b). When differences in the Sr concentration of each endmember decrease, the differences between concentration included and concentration excluded mixing models also decreases. This is observed in the results for the residual soil Sr mixing model, where dust concentration is set at 200 ppm and the basalt is set at 263 ppm (Appendix b, Figures 2a, b).
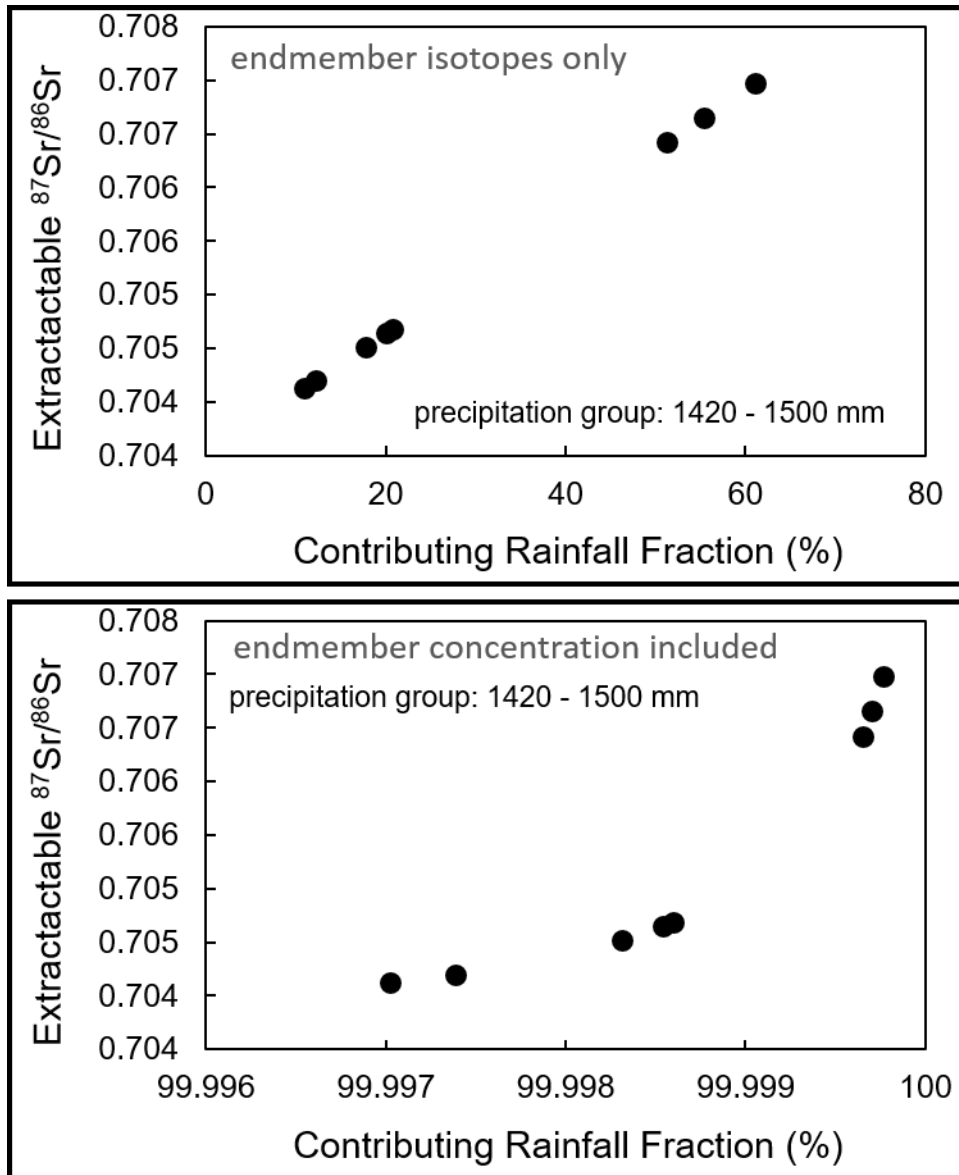
Figure 1. Rainfall-derived Sr contributed to the extractable soil fraction for wettest soils. (a) Fraction contributed by rainfall was calculated with a two endmember mixing model that includes endmember concentration. The rock endmember had an isotope signature of 0.7035 and a concentration of 263 ppm and the rainfall endmember had an isotope signature of 0.7092 and a concentration of 0.001 ppm. (b) Fraction contributed by rainfall was calculated with a two endmember mixing model that only used endmember isotopes. The rock endmember had an isotope signature of 0.7035 and the rainfall endmember had an isotope signature of 0.7092.
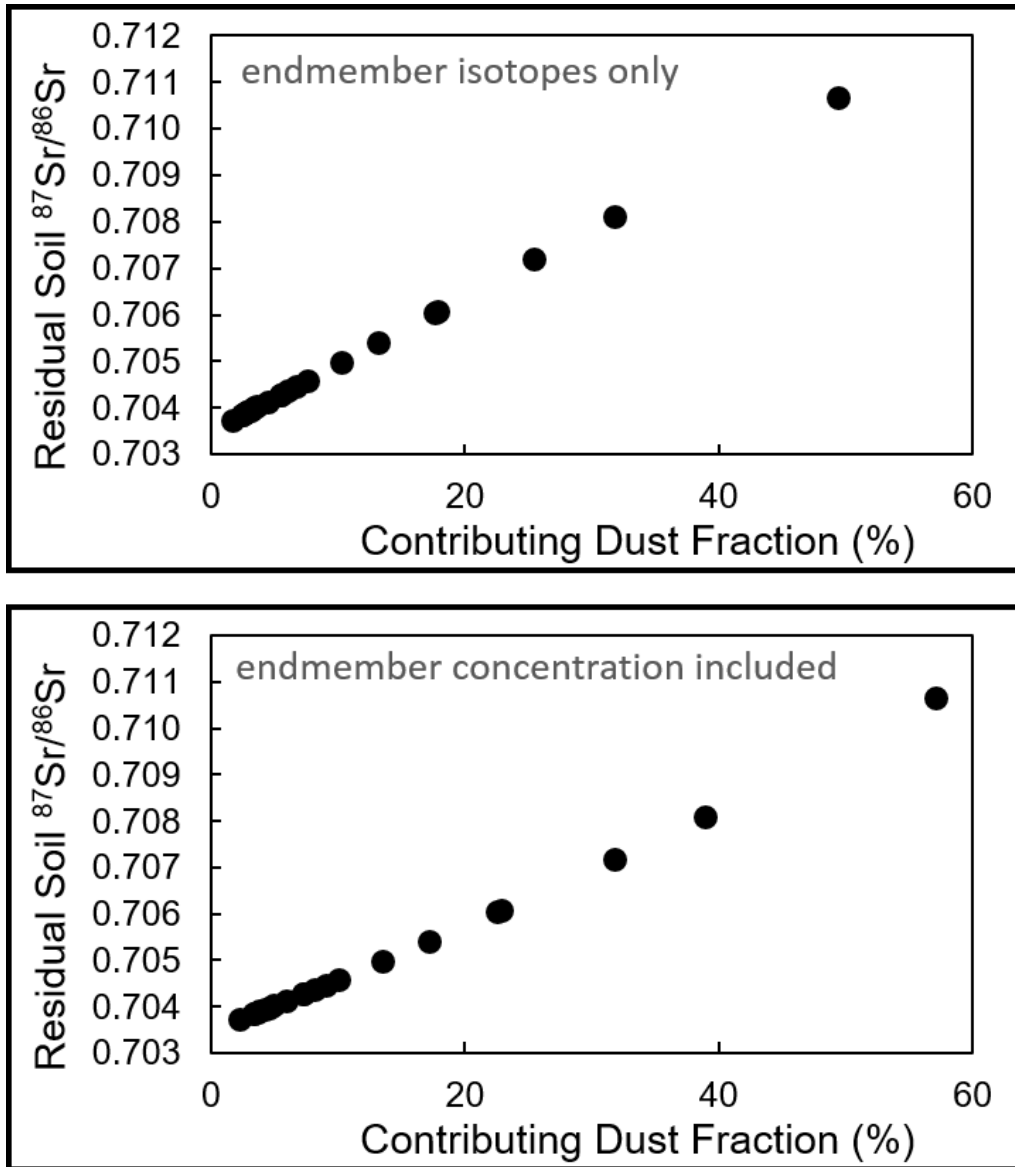
Figure 2. Dust-derived Sr contributed to the residual soil regardless of rainfall or age groupings calculated by a simple two endmember mixing model. (a) Fraction of residual Sr contributed by dust deposition using a mixing model which includes endmember concentration. The rock endmember had an isotope signature of 0.7035 and a concentration of 263 ppm Sr. The dust endmember had an isotope signature of 0.718 and a concentration of 200 ppm Sr. (b) Fraction of residual Sr contributed by dust deposition calculated with a two endmember mixing model only using endmember isotopes. The rock endmember had an isotope signature of 0.7035 and the rainfall endmember had an isotope signature of 0.718.

Testing for two-endmember mixing by checking linearity of the data in a Sr isotope vs 1/Sr concentration plot implies influence by the total concentration of an endmember on the isotopic signature. In other words, the two-endmember mixing model used if mixing is likely, will include endmember concentration in the model. Notice that the endmembers in my study do not bracket the data spread as to be expected if concentrations of each endmember directly influenced the isotopic values of the samples (Appendix b, Figures 3, 4). Continuation of this project could include perhaps time-independent concentrations of Sr calculated from the Sr flux by each source could be used as a mixing model endmembers for models which include endmember concentration. This model could produce more informative results which describe the flux of Sr from each source at any given time during soil formation in the Kona region.
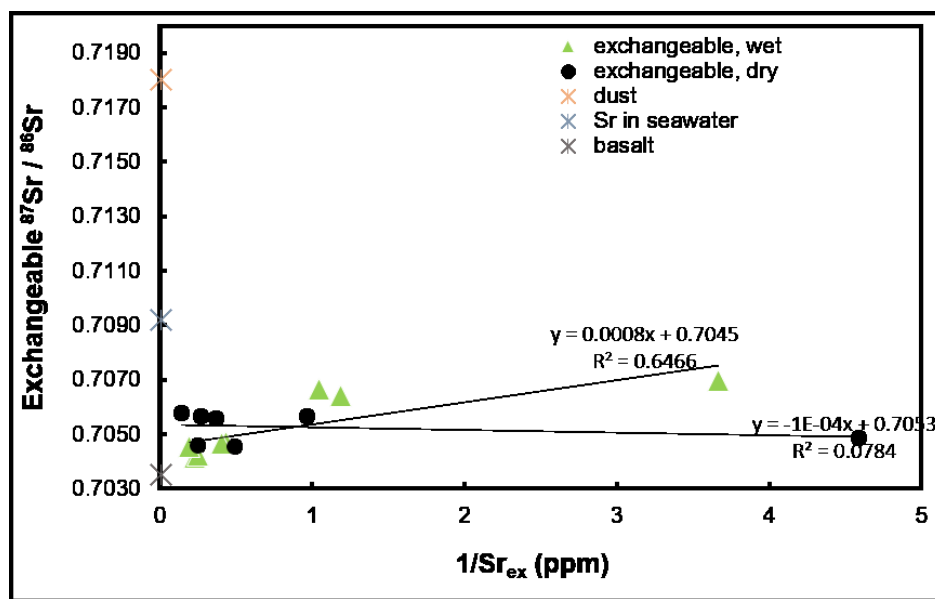

Figure 3. Extractable Sr isotope values compared to 1/[Sr] for the wettest soils and the driest soils, endmembers for mixing are also plotted. Strong linearity indicates two endmember mixing for the isotope values; based on R^2 values, this is likely the case for the wettest soils but not for the driest soils. The rainfall endmember is seawater influenced, thus the concentration of Sr in marine derived rainwater is calculated by multiplying the Sr concentration of seawater by the proportion of Sr to the total dissolved solids in seawater.
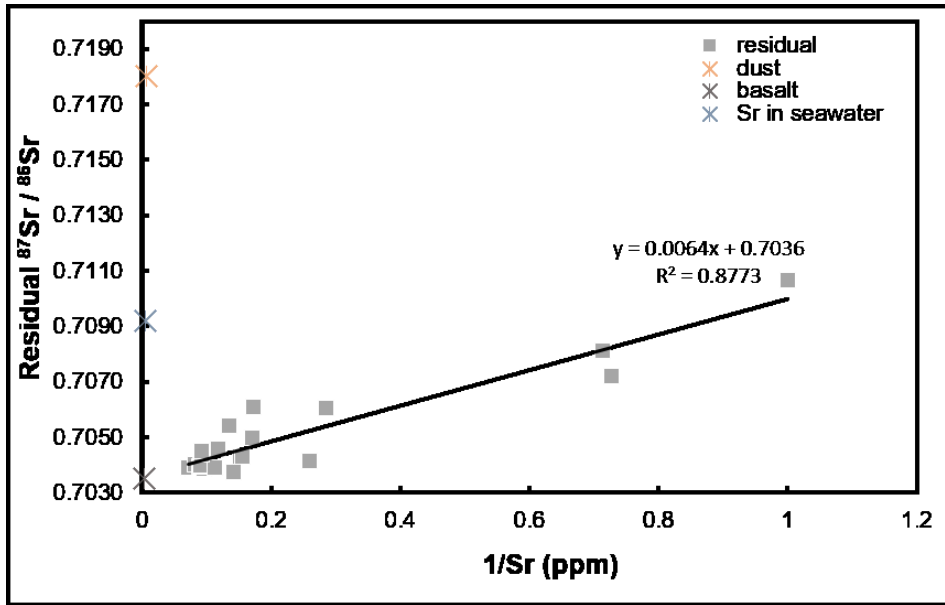
Figure 4. Strontium isotopes of the soil residue compared to the inverse concentration of Sr for these residual soils. The residual soils are strongly linear in normal space indicating two endmember mixing between basalt and an atmospheric source is likely. The rainfall endmember is seawater influenced, thus the concentration of Sr in marine derived rainwater is calculated by multiplying the Sr concentration of seawater by the proportion of Sr to the total dissolved solids in seawater.