GEOCHEMICAL INVESTIGATION OF FLUID-ROCK INTERACTIONS DURING CHEMICAL WEATHERING AND SUBDUCTION

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ABSTRACT

Heather Dawn Hanna: Geochemical Investigation of Fluid-Rock Interactions During Chemical Weathering and Subduction (Under the direction of Xiaoming Liu)

This research examines fluid-rock interactions in two significantly different environments. First, Li isotopic values are evaluated as a potential slab component tracer in Aleutian island arc rocks. The δ^7 Li values of Aleutian lavas do not exhibit the spatial trends observed in other slab component tracers, nor do they or correlate with these tracers. However, mixing models using δ^7 Li values in conjunction with ¹⁴³Nd/¹⁴⁴Nd ratios suggest most Aleutian samples can be explained by addition of <1-2% sediment-derived aqueous fluid and \leq 3% sediment melt to depleted mantle. The study demonstrates that slab signatures may be deciphered via modeling even in arcs where δ^7 Li values overlap.

Next the impact of weathering intensity and climate on basalt weathering and pedogenic processes are examined for soil and saprolite samples from San Cristobal island, Galapagos. This research suggests different mineralogical controls dominate element retention in different climate zones. When age is held constant, congruent weathering of olivine appears to dominate element retention in dry climates, with amorphous phases becoming important as humidity and weathering intensity begin to increase. Crystalline secondary phases, in particular gibbsite, become the dominant influence under high humidity and weathering intensity, while goethite and hematite strongly influence elemental retention in samples from older, drier climate. Additionally, Rare Earth Element (REE) distribution provides insight into variations in pedogenic processes under differing climate and weathering intensities. In dry to seasonally humid climates, the flux of REE-rich aqueous fluids into the profile from more weathered areas primarily controls REE distribution, with plagioclase leaching promoting REE precipitation and thus, REE-enrichment. Heavy REE (HREE) are more enriched than Light REE (LREE) in these samples. As humidity and weathering intensity increase, vertical translocation of elements within the profile becomes significant, and the leaching of elements ultimately outweighs any flux of REE into the profile. Under these conditions, all REE are depleted, with fluid mobile HREE more depleted than LREE.

To all the girls who dream of being scientists: you never know unless you try.

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LIST OF ABBREVIATIONS AND SYMBOLS

‰o	Per mil
±	Plus or minus
δ ⁷ Li	Delta 7 lithium
$\delta^{18}O$	Delta 18 Oxygen
τj	Percent mass change of an element during weathering
¹⁴³ Nd/ ¹⁴⁴ Nd	Neodymium isotope ratio
¹⁷⁶ Hf/ ¹⁷⁷ Hf	Hafnium isotope ratio
²⁰⁶ Pb/ ²⁰⁴ Pb	Lead isotope ratio
⁸⁷ Sr/ ⁸⁶ Sr	Strontium isotope ratio
Ce/Ce*	Cerium anomaly
Ce _N	Cerium normalized to parent composition
CHANL	Chapel Hill Analytical and Nanofabrication Lab
CHUR	Chondritic Uniform Reservoir
CIA	Chemical Index of Alteration
DSDP	Deep Sea Drilling Program
Eu/Eu*	Europium anomaly
Eun	Europium normalized to parent composition
Fe ₂ O ₃	Total iron as Fe ₂ O ₃
FeO*	Total iron as FeO
g/yr/cm	Grams per year per centimeter
GN	Gadolinium normalized to parent composition
HREE	Heavy Rare Earth Elements

ka	Kilo-annum (thousands of years)
(La/Lu) _{Parent}	Parent composition-normalized ratio of lanthanum to lutetium
LREE	Light Rare Earth Elements
Ma	Mega-annum (millions of years)
MIA	Mafic Index of Alteration
mm/yr	Millimeters per year
MORB	Mid-ocean ridge basalt
Nd _N	Neodymium normalized parent composition
°N	Degrees north
Pr _N	Praseodymium normalized to parent composition
Q-ICP-MS	Quadrupole Inductively Coupled Plasma Mass Spectrometer
REE	Rare Earth Elements
Smn	Samarium normalized to parent composition
°W	Degrees west
XRD	X-ray diffraction

CHAPTER 1: INTRODUCTION

This research examines how interactions between rock and fluid impact the chemistry of igneous rocks formed by subduction and weathering of ocean island basalt. The dissertation chapters focus on samples from two distinct locations: 1) rock samples from the Aleutian Islands, Alaska; and 2) soil, saprolite, and rock samples from San Cristobal island, Galapagos.

The second dissertation chapter focuses on using Li isotopes as a subducting slab component tracer in lavas and intrusive rocks from the Aleutian arc. Island arc lavas and intrusions contain chemical signatures that cannot be produced by melting of depleted mantle alone (e.g., Kay and Kay, 1994). Two components of the subducting slab, sediment and altered oceanic crust, have, in varying proportions, been implicated as the primary sources of these signatures. However, questions remain as to which components are present in lava from a given area, and whether those components are transported into the mantle wedge via melts, or by supercritical aqueous fluids (e.g., Kelemen et al., 2014).

Li isotopes have potential to be a good tracer for slab signatures in arc rocks. First, Li isotopes are fractionated by low temperature, surficial processes which can produce sediment and altered oceanic crust with very different Li isotope signatures from the mantle. Aside from the possibility of distinctive isotopic signatures, the behavior of Li as an element means it can be transported from the subducting slab into the overlying mantle. The high solubility of Li implies a slab signature could be transported by slab fluids, albeit a with a fractionated isotopic signature due to the preference of ⁷Li for the fluid phase. Additionally, Li behaves as a moderately

incompatible element during mantle melting, but Li isotopes are not fractionated by mantle melting (Tomascak et al., 1999). Therefore, Li isotopic signatures from sediment and/or altered oceanic crust melt could be transferred into the mantle and preserved in later-formed rocks.

Despite this potential, previous studies have yielded mixed and sometimes conflicting results when using Li isotopes to trace recycled subducting slab components. However, this study demonstrates that Li isotopes can be used in combination with radiogenic isotopes to identify sediment melt and fluid signatures, even in areas where trends between δ^7 Li values and other slab tracers are absent. Additionally, the Li isotope signatures of the subducting Aleutian sediment fall within the range of the mantle, showing large differences between sediment and mantle do not have to exist in order to decipher a recycled sediment signature.

The third and fourth chapters focus rock and soil samples collected from San Cristobal island, Galapagos. San Cristobal island is located on the easternmost side of the Galapagos island chain where the Nazca plate has moved off of the hotspot (Geist et al., 2008). An extinct shield volcano forms the southwestern portion of San Cristobal, providing the island's topographic high and the locations of this study's sampling sites. Compositionally, the island is almost entirely basalt, which ranges in age from 2.33 ± 0.13 Ma to an estimated <1,000 years (Geist et al., 1986). Most study samples were collected from areas where most lavas have been dated at ~781,000 years old (Geist et al., 1986). Due to the steep topography of the shield volcano, three microclimate zones are present over a small area. A dry zone is present in the lowlands, which receives a minimum of 500 mm/yr of precipitation; a transition zone mid-way up the shield volcano, which represents the soft boundary between dry and humid zones; and the humid zone, which is located at higher elevations and receives annual precipitation up to 1,500-2,000 mm/yr (Trueman and d'Ozouville, 2010, and references therein). The relatively uniform age and

composition of the shield volcano, combined with the different climate zones at different altitudes, allows for the source material to be held relatively constant while examining the effect of differences in rainfall and, by extension, degree of weathering.

The third chapter examines mineralogical controls on element retention during basalt weathering in different climate zones. Existing research has addressed the role of climate variations in secondary mineral formation (e.g., Chadwick et al., 2003), however, the influence of different climate conditions on mineralogical control of elemental behavior remains a knowledge gap. This research also examines non-weathering-related contributions, such as atmospheric dust, to San Cristobal profiles. The sources of eolian material to the Eastern Equatorial Pacific are less studied than other areas, and debate exists in the literature about the contribution of Australian and Northern Hemisphere sources (Xie and Marcantonio, 2012). This research provides insight into origin of eolian contributions through Nd isotopic signatures in San Cristobal samples.

The fourth chapter uses Rare Earth Elements (REE) to examine pedogenic processes occurring in the San Cristobal profiles. Traditionally, many REE studies have focused on a single profile, although chrono sequences and the impact of lithology have also been examined. However, the impact of climate and weathering intensity on REE distribution in soils is not well studied. An improved understanding of how different climate conditions and weathering intensities impact REE distributions can help fill knowledge gaps surrounding variations in pedogenic processes with climate. Finally, both chapters three and four promote a better understanding of soil composition on the island and help inform management decisions by the National Park.

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CHAPTER 2: LITHIUM ISOTOPES MAY TRACE SUBDUCTING SLAB SIGNATURES IN ALEUTIAN ARC LAVAS AND INTRUSIONS¹

1. Introduction

Arc lavas are well documented to be geochemically different from mid-ocean ridge basalts (MORB), with elevated incompatible trace elements and more enriched isotope ratios indicating that melting of MORB-source mantle alone cannot produce these lavas (Kay and Kay, 1994; Elliott, 2003; Kelemen et al., 2003). Two components of the subducting slab, sediment and altered oceanic crust, have, in varying proportions depending on the arc, been implicated as the primary sources of these non-MORB signatures (Elliott, 2003). However, questions remain as to which components are present in a given arc, and whether those components are transported into the mantle wedge via melts, or by supercritical aqueous fluids (Miller et al., 1994; Class et al., 2000; Elliott, 2003; Kelemen et al., 2014). Thus, a potential tracer should help differentiate the cause(s) of geochemical differences between MORB and arc lavas with respect to the influence of components from the subducting slab. Trace element and radiogenic isotope signatures are often used to examine the potential presence of slab components; however, their interpretation is not always straightforward, and as such, multiple types of data are often required. In particular, light stable isotope systems, such as Li, are of interest due to the large fractionation that occurs at Earth's surface (e.g., Penniston-Dorland et al., 2017, and references therein).

¹ Hanna, H.D., Liu, X-M., Park, Y-R., Kay, S.M., Rudnick, R.L. (2020) Lithium isotopes may trace subducting slab signatures in Aleutian arc lavas and intrusions. Geochimica et Cosmochimica Acta 278, 322-339.

Lithium is a moderately incompatible, water soluble, alkali metal present only in the +1 valence state. It has two isotopes, ⁷Li (92.4%) and ⁶Li (7.6%), and a large (~17%) relative mass difference resulting in significant fractionation of the two isotopes (Burton and Vigier, 2011; Tomascak et al., 2016; Penniston-Dorland et al., 2017). This fractionation is expressed relative to the L-SVEC lithium carbonate standard (Flesch et al., 1973) using the δ^7 Li notation: δ^7 Li (‰) = ([⁷Li/⁶Li]_{sample}/[⁷Li/⁶Li]_{standard}-1)×1000. Higher δ^7 Li values indicate a preference for ⁷Li relative to ⁶Li.

Temperature is known to have a significant impact on equilibrium Li isotope fractionation. Low temperature, near-surface weathering processes, particularly those involving fluid-rock interactions (Chan et al., 1992; Chan et al., 2002a; Pistiner and Henderson, 2003), are the dominant causes of equilibrium Li isotope fractionation and produce a span in δ^7 Li of over 50‰ (see review of Penniston-Dorland et al., 2017). Secondary mineral formation is a major cause of this fractionation, with ⁶Li preferentially incorporated into the mineral while ⁷Li remains in the fluid phase (Rudnick et al., 2004; Teng et al., 2010; Liu et al., 2013; Liu et al., 2015). In contrast, high temperature equilibrium igneous processes, such as mantle melting and fractional crystallization of basalts cause insignificant Li isotope fractionation (Tomascak et al., 1999), though fractionation may occur during the latest stages of evolution of granitic systems (Teng et al., 2006). High temperature metamorphic processes, such as metamorphic dehydration (Marschall et al., 2007; Teng et al., 2007; Qiu et al., 2009; Qiu et al., 2011a; Qiu et al., 2011b) also produce very minimal isotopic fractionation. Thus, Li isotope compositions of igneous rocks that deviate beyond the range of mantle-derived basalts (+1.6 to +5.6; Penniston-Dorland et al., 2017) usually reflect the influence of low temperature fluid-rock interactions. The non-MORB δ^7 Li values may be caused by post-crystallization alteration or may be inherited from an altered

source. Kinetic fractionation can occur at high temperatures and produce significant Li isotope fractionation (e.g. ~40‰ in a study by Richter et al., 2003) because ⁶Li diffuses up to 3% faster than ⁷Li in a silicate melt and water (Flesch et al., 1973; Lundstrom et al., 2005; Richter et al., 2006). However, given the scale of processes examined in this study, equilibrium fractionation is expected to be the dominant influence.

The potential to use Li isotopes as tracers for subduction zone processes was realized when Chan et al. (1992) noted that Li isotopes are strongly fractionated during basalt-seawater interaction. This interaction could produce δ^7 Li signatures in altered oceanic crust significantly different from those of the mantle (e.g., Penniston-Dorland et al., 2017 and references therein). The same potential applies to subducted sediment input, especially in arcs where there is a significant component of highly weathered terrigenous sediment being subducted (e.g., the Lesser Antilles island arc, Tang et al., 2014). Aside from the possibility of distinctive isotopic signatures, the behavior of Li as an element (incompatible and water-soluble) means it can be transported into the mantle wedge by slab-derived fluids and, if present, slab-derived melts. The high solubility of Li implies a slab signature could be transported by slab fluids, albeit with a fractionated isotopic signature due to the preference of ⁷Li for the fluid phase. Because Li behaves as a moderately incompatible element during mantle melting, and Li isotopes are not fractionated by mantle melting (Tomascak et al., 1999), high temperature processes should not obscure the low temperature signature. Therefore, Li isotopes have the potential to be good tracers for recycling of slab components in arc settings.

The existence of isotopically fractionated slab-derived fluids, sediment, and altered oceanic crust has been previously documented in arc lavas (Chan and Kastner, 2000; Chan et al., 2002a; Chan et al., 2006; Agostini et al., 2008; Bouvier et al., 2008; Tang et al., 2014). The δ^7 Li

values of fresh mid-ocean ridge basalt (MORB) (+1.6 to +5.6%; Penniston-Dorland et al., 2017) are taken to reflect the range of depleted mantle values, and slab fluids are expected to have a heavy Li isotopic signature compared to the mantle (Tang et al., 2014 and references therein). The latter is supported by fore-arc seamount fluids with δ^7 Li as high as ~+20‰ that are interpreted to derive from the subducting slab (Chan and Kastner, 2000; Tang et al., 2014). In contrast to the heavy fluid signature, subducting sediments span a wide range of $\delta^7 Li$ values (-1.1 to +9.4‰; Chan et al., 2006; Plank, 2014) extending to both lighter and heavier values compared with the mantle range. Melt from altered oceanic crust could also contribute a wide range of $\delta^7 Li$ values to the mantle, as δ^7 Li of altered MORB (-1.7‰ to +20.8‰) extends to more positive and negative values than fresh MORB (Chan et al., 1992; Chan et al., 2002a; Bouman et al., 2004; Brant et al., 2012) due to the effects of hydrothermal leaching and secondary mineral growth, which can decrease and increase δ^7 Li values, respectively. Chan et al. (2002a) noted depthdependent variations in δ^7 Li values of altered oceanic crust, wherein the highest δ^7 Li values were recorded in the upper portion of the volcanic section, which was underlain by a transition zone of isotopically light values before reaching unaltered MORB. Penniston-Dorland et al. (2017) calculate an average altered MORB value of $5.6 \pm 4.5\%$.

The Aleutian arc provides an ideal location to investigate the use of Li isotopes as a tracer for slab-derived components. It contains the type locality for adakites (Adak Island), which were initially interpreted to derive from partial melting of the subducted oceanic crust (eclogite; Kay, 1978), however, more recent work indicates this eclogite component may be due to subduction erosion of the mafic forearc (e.g., Kay, 2003; Jicha and Kay, 2018). Additionally, the Aleutian Arc was one of the first arcs identified as having a subducted sediment signal (Kay, 1980), and has the highest calculated sedimentary Li flux (18 g/yr/cm) of any arc examined by Chan et al.

(2006). The subducting sediment in the Aleutian trench has a mass weighted mean δ^7 Li value of 2.0‰ (Chan et al., 2006), and while that value falls on the lowest end of the mantle range, it may still be light enough to allow a sedimentary signature to be resolved. Finally, the well-characterized Aleutian samples studied here allow lithium isotopic signatures to be compared to existing slab component parameters to determine whether Li isotopes reflect fluid, slab melt, and/or sediment melt signatures already identified in some of the samples (Kay, 1978; Kay, 1980; Miller et al., 1994; Class et al., 2000; Yogodzinski et al., 2010).

2. Geological Setting and Samples

The Aleutian island arc is located on the northern rim of the Pacific basin west of the ocean-continent transition (George et al., 2003). Here, the ~ 50 Ma Pacific plate subducts beneath the Bering plate at the Aleutian trench (Figure 2.1; Jicha and Kay, 2018). Because of the Aleutian arc's shape, convergence is nearly normal in the east, becoming oblique near Adak island, and ultimately forming a nearly strike-slip boundary in the far western reaches of the arc (Vallier et al., 1994). The orthogonal convergence rate also decreases from ~60-75 mm/yr from Adak east to <40 mm/yr in the far western reaches of the arc (Fournelle et al., 1994).

The Aleutian arc can be divided into three sections (Figure 2.1). The eastern Aleutians are located east of 164°W (Kelemen et al., 2003). Geochemically, these volcanoes could be influenced by continental crust from the Alaskan peninsula and are not included in this study. The central Aleutians, located from 164 °W to Bowers Ridge, represents a classic oceanic arc composed mainly of tholeiitic basalts and their differentiation products (Kelemen et al., 2003). The western Aleutians, located west of Bowers Ridge (Figure 2.1, Kay et al., 1982), contain a

mix of tholeiitic basalts and calc-alkaline andesites, with calc-alkaline lavas becoming dominant toward the western portion of the segment (Kelemen et al., 2003).

Aleutian trench sediments are largely turbidites composed of detritus from the Alaskan range and the Chugach, Wrangell, and Saint Elias Mountains, but show an increase in the proportion of pelagic relative to continentally-derived sediment in the western arc (between 182 to 190°W; see Kay and Kay, 1994, for discussion). According to geophysical data, Aleutian trench sediments gradually thicken from ~900 m near 160°W to over 1400 m around 172°W, then gradually thin again west of 172°W (Kelemen et al., 2003). A well-studied Deep Sea Drilling Program (DSDP) core (Site 183) is located at 52.57°N, 161.20°W on the northern edge of the Alaska Abyssal Plain (Figure 2.1) and provides a bulk estimate of Aleutian trench sediment. The base of the core is composed of 253 m of turbidites with silt and clay (plus a thin, 4 m limestone horizon at the very base). The turbidite sequence is overlain by 38 m of pelagic clay + chalk, which, in turn, is overlain by 210 m of ash-rich diatomaceous ooze (Chan et al., 2006). Plank and Langmuir (1998) provided major and trace element concentrations and radiogenic isotope ratios for DSDP Site 183 sediments, with some trace element values updated by Plank (2014) using data from Chan et al. (2006) and Vervoort et al. (2011). Chan et al. (2006) analyzed Li isotopes for the sedimentary units, the δ^7 Li values of which range from +1.3‰ for clay and silt horizons to $\delta^7 \text{Li} + 5.6\%$ for the diatomaceous ooze, with a mass weighted mean of +2.0‰ for the entire core. While the nature of subducting sediment varies from dominantly terrigenous in the east, to an increasing pelagic component in the west (e.g., Yogodzinski et al., 2010), Chan et al. (2006) were unable to distinguish between pelagic and terrigenous sediments based on δ^7 Li values.



Figure 2.1. Map of the Aleutian Arc and its location relative to portions of North America and Asia. Volcanoes and plutons with samples included in this study are noted with red stars. Location of DSDP Core Hole 183 is also shown on the map.

This paper presents Li concentrations and isotopic signatures for 31 lavas and 17 intrusive samples from the Central and Western Aleutians. Tomascak et al. (2002) published Li concentration and isotopic data for an additional four Aleutian lavas in their global-scale study of Li in island arcs. This research has incorporated those data, but greatly expands on the number and geographic distribution of Aleutian samples in order to examine potential spatial relationships. The sample suite incorporates lavas from 11 volcanic centers as well as three intrusive bodies (Figure 2.1) that span a geographic range from 165°W to 184°W, a compositional range from 46 to 70 wt.% SiO₂, and an age range from <1 Ma to 38 Ma. The intrusive samples are from the Hidden Bay and Finger Bay plutons on Adak Island, and the Kagalaska pluton on Adak and Kagalaska Islands, and range in age from 14 to 38 Ma (Kay et al., 2019).

Major and trace element compositions are published for all samples, and radiogenic isotopes and δ^{18} O data are available for many samples (Walker, 1974; Arculus et al., 1977; Kay, 1977; Kay, 1978; Kay et al., 1978; Sun, 1980; Kay et al., 1983; Kay et al., 1986; Neuweld, 1987; Kay et al., 1990; Miller et al., 1992; Kay and Kay, 1994; Class et al., 2000; George et al., 2003; Kelemen et al., 2003; Munker et al., 2004; Yogodzinski et al., 2010; Yogodzinski et al., 2015; Nielsen et al., 2016; Kay et al., 2019), providing the opportunity to compare Li isotopic signatures to a variety of inferred proxies for fluid, slab melt, and sediment melt components. A compilation of these previously published results is provided in Appendix 1.

3. Methods

Lithium isotope values and lithium concentrations were analyzed for a suite of 48 Aleutian sample powders studied by Kay and Kay (1994), or prepared from whole rock samples. Whole rock samples were cut and then pulverized using an alumina jaw crusher after any weathered/altered surfaces of samples were sawn off. All preparation and analyses were conducted at the Geochemical Laboratory of the University of Maryland. The method of lithium isotope analysis used here was previously described in Liu et al. (2010; 2013) and follows from that originally described by Moriguti and Nakamura (1998a). A brief description of sample dissolution, column chemistry and instrumental analysis is provided below.

For each sample, between 20 to 100 mg of rock powder was dissolved using a ~ 3:1(v/v) mixture of HF and HNO₃ in Savillex® screw-top beakers on a hot plate (T ≈ 90°C), followed by twice HNO₃ and once HCl addition until all powder was dissolved and the final solution was clear. Final solutions in 4M HCl were then purified using four-step cation exchange columns (BioRad AG50W-x12, 200-400 mesh). The first two columns eliminate major cations in samples using 2.5M HCl and 0.15M HCl, respectively. The third column separates Na from Li using 30% ethanol in 0.5M HCl and the fourth column is a repeat of the third to further separate Na from final solution for instrumental analysis. Yields from the chromatography were determined to be greater than 95% (Marks et al., 2007). Finally, Li solutions (~ 50 ppb Li in ~2% HNO₃) were analyzed using a Nu Plasma Multi Collector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS). Standard bracketing, using L-SVEC (Flesch et al., 1973), was performed for all analyses. Li concentrations were determined from Li intensity during isotopic measurements compared to that of the standard (precision is <10%, 1 σ ; Teng et al., 2004). The external precision of δ^7 Li, based on 2 σ of duplicate runs of pure Li standard solutions, is $\leq \pm 1.0$ %. For

example, repeat analyses of two pure Li solutions, analyzed during the course of this study yield the following results: an in-house standard, UMD-1, a purified Li solution from Alfa Aesar[®], gives $\delta^7 \text{Li} = +55.1 \pm 0.7\%$ (2 σ , n = 21) and IRMM-016 (Qi et al., 1997) gives $\delta^7 \text{Li} = 0.2 \pm$ 0.9‰ (2 σ , n = 23). In addition, several USGS rock standards were run repeatedly (Table A2.1 in Appendix 2). BHVO-1 yielded $\delta^7 \text{Li}$ of 4.8 ± 0.1 (n= 2) cf. 4.0 to 5.6 in the literature (GeoReM database: <u>http://georem.mpch-mainz.gwdg.de/</u>); and BCR-1 yielded $\delta^7 \text{Li}$ of 2.9 ± 1.1 (n = 2) cf. 2.0 to 3.0 in the literature (GeoReM database).

It should be noted that flux-dissolution methods, which commonly use Li as a major constituent, cannot be used in Li isotope analyses. Even a small amount of lithium metaborate flux can contaminate powders and drastically impact Li isotope measurements, making it is advisable to carry out all sample preparation for Li isotopes in a laboratory where such fluxes are not in use. Most commercially available Li is enriched in ⁷Li due to extraction of ⁶Li for other purposes (e.g., the Alfa Aesar[®] Li solution mentioned above). Thus, most examples of sample contamination due to inadvertent addition of Li flux increases the δ^7 Li of the sample. An example of this contamination was noted during collection of data in this study. A powder of gabbro from the Finger Bay Pluton came from a laboratory where Li metaborate fluxes were in use. The measured Li concentration and isotopic composition of this powder were 10.7 ppm and +28‰, respectively. Rocks with such a high δ^7 Li are rare. To investigate whether this unusual isotopic composition was due to Li metaborate flux contamination, eight fresh powders from original rocks, including the Finger Bay Pluton sample, were prepared at University of Maryland where Li metaborate fluxes are not used. All newly prepared powders yielded the sample Li concentration and isotopic composition as previously determined on the original powders, within the analytical uncertainty, with one exception: the Finger Bay Pluton sample, where the newly

prepared powder had Li concentration and δ^7 Li values of 9.6 ppm and +0.7‰, respectively. The addition of a very small amount of Li flux in the original powder increased the Li concentration by 1 ppm or ~10%, which falls within the uncertainty of measurement for Li concentration but had a significant impact on the Li isotopic composition of the sample due to the presumed extreme Li isotopic composition of the flux (see detailed description in electronic supplement of Penniston-Dorland et al., 2017).

4. Results

 $δ^7$ Li values for 32 of the 35 lavas and 12 of the 17 intrusive samples fall within the MORB range (Table 2.1a and b). Two lavas (-0.7 and +0.5‰) and one intrusive sample (+0.7‰) exhibit values lower than the MORB range, while one lava (+8.4‰) and five intrusive samples (+5.9, +6.9, +7.2, +7.7, and +14.2‰) exhibit higher values (Figure 2.2). To reveal any subtle variations that may not be obvious from the data set as a whole, samples were evaluated based on geochemical series (Kay and Kay, 1994), composition (basalt, basaltic andesite, andesite, etc.), and volcanic center. Examining the data by geochemical series and composition did not reveal any trends, and examining the data by volcanic center was not very informative because some volcanoes had two or fewer data points. Thus, data are grouped into "lavas" and "intrusions" in this paper. To evaluate the possibility of post-eruption weathering affecting lithium isotope signatures, $δ^7$ Li values of Aleutian samples are plotted against the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982) and the Mafic Index of Alteration (MIA; Babechuk et al., 2014) , since loss on ignition (LOI) data were not available for many samples (Figure 2.3). CIA is the molar ratio of [Al₂O₃/(Al₂O₃+CaO+Na₂O+K₂O)]*100, while MIA is the molar ratio of

Sample	Latitude (N)	Longitude (W)	Lithology	Li (ppm)	δ ⁷ Li				
Mount Westdahl, Unimak Island									
SAR11	54.556	164.761	Basaltic andesite	7.07	2.2				
SAR4	54.556	164.761	Trachydacite	18.26	2.4				
Bogoslof Island									
1927*	53.93	168.03	Basalt	5	2.3				
Mount Okmok, Umnak Island									
QAF-70*	53.42	168.13	Basalt	9.79	2.8				
UM10	53.42	168.13	Basalt	4.83	4.1				
UM11	53.42	168.13	Basaltic andesite	4.79	5.7				
UM22	53.42	168.13	Basalt	6.09	3				
UM4	53.42	168.13	Basalt	5.57	4.6				
UM5	53.42	168.13	Basaltic andesite	11.83	3.6				
UM16	53.42	168.13	Basaltic andesite	10.08	3.3				
Mount Recheshnoi, Umnak Island									
LUM-17*	53.367	169.183	Andesite	22.57	3.9				
LUM-21*	53.583	169.283	Basalt	9.22	3.2				
Islands of Four Mountains									
FMI-8	53.07	169.77	Andesite	11.57	2.9				
FMI-7	52.9	170.05	Andesite	12.67	2.5				
FMI-6	52.82	169.95	Rhvolite	16.49	2.4				
FMI-5	52.75	170.12	Andesite	8.45	8.4				
Yunaska Island									
FMI-2	52.65	170.76	Andesite	13.56	3.6				
Great Sitkin Volcano, Great Sitkin Island									
SIT-RK4	52.08	176.13	Trachydacite	16.3	5.6				
GS721B	52.08	176.13	Andesite	11.13	2.7				
GS723	52.08	176.13	Andesite	13.5	5.1				
GS727	52.08	176.13	Basalt	7.93	-0.7				

Table 2.1a. δ^7 Li values and Li concentrations for Aleutian Lavas

Sample	Latitude (N)	Longitude (W)	Lithology	Li (ppm)	δ ⁷ Li			
Mount Adagdak, Adak Island								
ADG14	51.99	176.587	Basalt	10.79	0.5			
ADG2	51.99	176.587	Andesite	10.78	2.1			
ADG7A	51.99	176.587	Basalt	5.23	1.6			
ADG8	51.99	176.587	Andesite	9.48	4.7			
Mount Moffett, Adak Island								
MOF81-17	51.93	176.75	Basaltic andesite	5.83	5.1			
MOF81-56A	51.93	176.75	Andesite	9.37	1.8			
MOF81-15	51.93	176.75	Basalt	5.73	1.8			
MOF81-44	51.93	176.75	Andesite	9.12	3.8			
Older Flow Under Mount Moffett Flows, Adak Island								
MOF53A (ADK-53)	51.93	176.75	High-Mg andesite	7.2	3.7			
Bobrof Island								
BO9-6A	51.9	177.43	Andesite	9.92	4.1			
BO9-8A	51.9	177.43	Basaltic andesite	6.69	3.1			
Buldir Island								
BUL4D	52.37	184.02	Basaltic andesite	12.75	2.7			
BUL6A	52.37	184.02	Andesite	13.8	4.3			
BUL6B	52.37	184.02	Basaltic andesite	7.24	5.5			

Table 2.1a. δ^7 Li Values and Li Concentrations for Aleutian Lavas, Continued
Sample	Latitude (N)	Longitude (W)	Lithology	Li (ppm)	δ ⁷ Li
Hidden Bay pluton, Adak Island					
HB5-137	51.6953	176.7167	Silicic Granodiorite	5.34	7.7
HB5-193	51.7101	176.6216	Diorite	12.99	2.3
HB7-10	51.7243	176.7138	Gabbro	9.2	4.7
BW7-28	51.6953	176.7167	Feldspar Porphyry	15.19	2.7
HB5-160	51.7235	176.632	Diorite	8.17	4.4
HB7-16	51.7181	176.6927	Porphyric Diorite	5.69	5.1
Mafic dyke cutting Hidden Bay Pluton and older host rock					
BW8-55	51.6953	176.7167	Dike	18.52	2.4
HB6-83J	51.7184	176.6529	Dike	10.6	7.2
Finger Bay pluton, Adak Island					
FB53	51.831	176.588	Gabbro	2.95	3.2
FB44	51.831	176.588	Gabbro	3.12	5.9
FB97	51.831	176.588	Gabbro	9.5	0.7
Kagalaska pluton, Kagalaska and Adak Islands					
Kag7-50	51.829	176.429	Gabbro	2.2	4.3
Kag7-32	51.808	176.437	Granodiorite	6.83	3.8
Kag7-1A	51.818	176.431	Granodiorite	8.34	6.9
Kag7-19B	51.837	176.438	Mafic Granodiorite	9.54	5.5
Kag7-44	51.833	176.456	Basaltic Dike	4.12	1.4
Gabbro Xenolith, Great Sitkin Island					
GS725B	52.08	176.13	Gabbro xenolith	2.79	14.2

Table 2.1b. δ^7 Li Values and Li Concentrations for Aleutian Intrusions

 δ^7 Li values and Li concentrations from Tomascak et al. (2002)



Figure 2.2. Range of δ^7 Li values in Aleutian lavas compared to published values for other arc lavas. Gray field indicates δ^7 Li range for MORB. Global arc lava data sources from Tang et al. (2014), with addition of data from Brens et al. (2019).

 $[(Al_2O_3+Fe_2O_3(T))/(Al_2O_3+Fe_2O_3(T)+MgO+CaO+Na_2O+K_2O)]*100.$ All samples have CIA values < 50 and MIA values <52 suggesting they are unweathered. No trends exist between δ^7 Li values and either of the weathering/alteration parameters for lavas or intrusions. Three of the five intrusions with δ^7 Li > MORB range have higher MIA values than the majority of intrusive samples, however, these samples also have higher SiO₂ concentrations, and Aleutian data show a positive correlation between MIA and SiO₂, suggesting a compositional influence is present. Lavas and intrusions show significant overlap in CIA, while lavas plot to a higher average MIA value than intrusions.

The δ^7 Li values of lavas and intrusions are plotted against longitude to examine whether along-arc variability exists. No systematic along arc variations are observed (Figure 2.4). However, the greatest variability in δ^7 Li values occurs between 176 and 177°W, with the highest (+14.2‰) and lowest (-0.7‰) samples both collected from Great Sitkin Island (176.13°W). The other two data points with δ^7 Li below the MORB range were collected from the Holocene Mount Adagdak (+0.5‰) and the Eocene Finger Bay pluton (+0.7‰), both of which are on Adak Island (176.59°W). Even when considering only samples with δ^7 Li within the MORB range, the 176 to 177°W arc segment still spans a slightly wider range of δ^7 Li (+1.6 to +5.6‰) than other areas sampled in this study. Lavas were also examined for trends in δ^7 Li versus distance from the trench (Figure A2.1a in the Appendix 2) and depth to the Wadati-Benioff Zone (Figure A2.1b) using the depth values of Syracuse and Abers (2006), however, no correlations were found. Values for these parameters were not available for intrusive samples and would be hard to calculate due to the northward migration of the arc since the Eocene (Kay et al., 2019).

Aleutian lavas in this study do not exhibit correlations between δ^7 Li values and any radiogenic isotopes (Figures 2.5a through c). The ¹⁴³Nd/¹⁴⁴Nd ratios of Aleutian lavas fall closer to the depleted mantle values than to the sediment values (Figure 2.5a). The lava with δ^7 Li > the MORB range has Nd isotope ratios slightly closer to sediment values than all other lavas except the backarc lava (1927 from Bogoslof Island; see Electronic Annex for data). The sample with the lowest δ^7 Li value falls well within the Nd isotopic range of the rest of the samples, while ¹⁴³Nd/¹⁴⁴Nd ratios were not available for the second lowest δ^7 Li lava. Nd isotope data are available for select Aleutian intrusive samples, and ¹⁴³Nd/¹⁴⁴Nd for these samples show an



Figure 2.3. Plot of δ^7 Li in Aleutian lavas and intrusions versus a. Chemical Index of Alteration and b. Mafic Index of Alteration. δ^7 Li error bar (2 sigma) for Aleutian samples is ±1.0‰. See text for definition of CIA and MIA.



Figure 2.4. Plot of δ^7 Li in Aleutian lavas and intrusions versus longitude. δ^7 Li error bar for Aleutian samples is ±1.0‰. Symbols as in Figure 2.3.

overall trend of increasing δ^7 Li values with decreasing ¹⁴³Nd/¹⁴⁴Nd (Figure 2.5a). Some of the intrusions overlap with ¹⁴³Nd/¹⁴⁴Nd of the lavas, while others fall to more radiogenic values. Two of the three intrusive samples with δ^7 Li > the MORB range fall to slightly higher ¹⁴³Nd/¹⁴⁴Nd than the rest of the intrusions, while the sample with δ^7 Li < the MORB range falls within the range of ¹⁴³Nd/¹⁴⁴Nd of the rest of the intrusive samples.

Like ¹⁴³Nd/¹⁴⁴Nd, the ¹⁷⁷Hf/¹⁷⁶Hf of most lavas fall closer to depleted mantle values than to sediment values, clustering near the global MORB average (Figure 2.5b). The lava with δ^7 Li > MORB falls slightly closer to sediment Hf isotope values than all samples except the backarc sample, while the lowest δ^7 Li sample falls well within the ¹⁷⁷Hf/¹⁷⁶Hf range of the rest of



Figure 2.5. Plot of δ^7 Li versus a. ¹⁴³Nd/¹⁴⁴Nd b. ¹⁷⁶Hf/¹⁷⁷Hf. Nd and Hf isotope ratios for Global MORB from White and Klein (2014); δ^7 Li values from Penniston-Dorland et al. (2017). DSDP Core 183 average values for δ^7 Li (2.0‰; Chan et al., 2006) and Nd and Hf isotope ratios (Plank, 2014) are used for the sediment melt. ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf ratios for Aleutian lavas from Yogodzinski et al. (2010); ¹⁴³Nd/¹⁴⁴Nd ratios for Aleutian intrusions from Kay et al. (1983); Kay et al (1990); and Kay et al. (2019). Average depleted mantle δ^7 Li value from Penniston-Dorland et al. (2017); Nd and Hf isotope ratios from Yogodzinski et al (2010); δ^7 Li error bar for Aleutian samples is ±1.0‰. Error bar for average MORB δ^7 Li value is ± 0.7‰ and smaller than the symbol.



Figure 2.5, continued. Plot of δ^7 Li versus c. ²⁰⁶Pb/²⁰⁴Pb and d. δ^{18} O. Pb isotope ratios and δ^{18} O values for Global MORB from White and Klein (2014); δ^7 Li values from Penniston-Dorland et al. (2017). DSDP Core 183 average values for δ^7 Li (2.0‰; Chan et al., 2006) and Pb isotope ratios (Plank, 2014) are used for the sediment melt. ²⁰⁶Pb/²⁰⁴Pb isotope ratios for Aleutian lavas are from Kay (1978); Kay et al. (1978); Class et al. (2000); Kelemen et al. (2003); Yogodzinski et al. (2015); and Nielsen et al. (2016); δ^{18} O values for Aleutian lavas are from Kay and Kay (1994). Average depleted mantle δ^7 Li value from Penniston-Dorland et al. (2017) and Pb isotope ratios from Workman and Hart (2005). Gray box in 5d indicates MORB range for δ^{18} O (Eiler, 2001) and δ^7 Li (Penniston-Dorland et al., 2017). δ^7 Li error bar for Aleutian samples is ±1.0‰. Error bar for average MORB δ^7 Li value is ± 0.7‰ and smaller than the symbol. Symbols same as in part a.

the samples. Hafnium isotopes are not available for intrusions, or for the second lowest δ^7 Li lava. The ²⁰⁶Pb/²⁰⁴Pb ratios of most lavas form trends between depleted mantle and average Aleutian sediment, with the highest δ^7 Li sample falling closer to the sediment ²⁰⁶Pb/²⁰⁴Pb ratio than any sample other than the backarc lava (Figure 2.5c). No Pb isotope data are available for the second lowest δ^7 Li sample or for most of the intrusive samples in this study.

Aleutian lavas for which there is published oxygen isotope data do not exhibit a trend between δ^7 Li and δ^{18} O (Figure 2.5d). Most samples fall beyond the MORB range for δ^{18} O values (5.4‰ to 5.8‰; Eiler, 2001) but within the MORB range for δ^7 Li values. The lava with δ^7 Li > the MORB range falls within the range of δ^{18} O values for the other Aleutian lavas. The two lavas with δ^7 Li < MORB do not have published oxygen isotope data, nor do the intrusive samples.

Finally, Li isotopic compositions are plotted against trace element proxies for sediment melt (Th/La and Th/Nd; Figure 2.6a and b), eclogite melt (Sr/Y and La/Yb; Figure 2.7a and b) and fluids (Li/Y and Cs/La; Figure 2.8a and b). Use of trace element ratios to identify slab components is generally applied only to lavas with less than ~56 wt.% SiO₂ because partition coefficients of the ratioed elements begin to diverge at higher extents of fractionation (Elliott, 2003; Tang et al., 2014), and more evolved samples may reflect magma mixing and crustal assimilation prior to eruption. Thus, the data set was significantly reduced in number, with 20 lavas and 11 intrusive samples remaining once more evolved samples were removed. All Aleutian samples with δ^7 Li values < MORB were primitive enough to remain in the data set, while three of the five intrusions with δ^7 Li > MORB also remained.



Figure 2.6. Plot of δ^7 Li versus a. Th/La and b. Th/Nd. Average δ^7 Li value of 2.0‰ for DSDP Core 183 from Chan et al. (2006); Th, La, and Nd concentrations for DSDP Core 183 sediment melt are from Singer et al (2007). Global MORB Li isotope value from Penniston- Dorland et al. (2017); trace element values are from White and Klein (2014). Th, La, and Nd Figure 2.6. continued, values of Aleutian samples from Kay et al. (1983); Kay et al. (1990); Kay and Kay (1994); Class et al. (2000), Yogodzinski et al. (2015), and Kay et al. (2019). δ^7 Li error bar for Aleutian samples is ±1.0‰.

Figures 2.6a and 2.6b show δ^7 Li values for Aleutian samples plotted against the Th/La and Th/Nd ratios, which are sensitive to the addition of melts from subducting sediments (Plank, 2005; Singer et al., 2007; Plank, 2014). Included for reference on the diagrams are a modeled Aleutian sediment melt composition from Singer et al. (2007) and the melted average mantle composition, as represented by the average global MORB trace element values of White and Klein (2014) and the global MORB δ^7 Li value from Penniston-Dorland et al. (2017). Aleutian lavas plot between the two end members despite scatter in the δ^7 Li values, though they cluster closer to the MORB end member, and do not show a correlation between δ^7 Li values and either Th/La or Th/Nd. Aleutian intrusions overlap with the lava field, but, on average, plot to lower Th/La and Th/Nd for a given δ^7 Li value. Kay et al. (2019) also note lower Th/La ratios in the plutons relative to the younger Adak volcanic samples. Intrusive samples show an overall positive relationship between δ^7 Li and Th/Nd. A weak correlation between δ^7 Li values and Th/La may also exist in the intrusion data, however, the correlation rests largely on one sample. The sample with the highest δ^7 Li values, a gabbroic xenolith from Great Sitkin, also has the highest Th/Nd and Th/La ratios, while the other two intrusive samples with δ^7 Li values > MORB fall within the trace element range of the other intrusions. The three samples with δ^7 Li values < MORB have Th/La and Th/Nd ratios within the range of the majority of the samples.

Figures 2.7a and 2.7b show δ^7 Li values for Aleutian samples plotted against trace element indicators of eclogite melts, namely Sr/Y and La/Yb. Included for reference are the average global MORB values of White and Klein (2014) and Penniston-Dorland et al. (2017), and a proposed slab melt composition from Kelemen et al. (2003). Aleutian lavas plot roughly between the two end members, despite scatter in the δ^7 Li values, clustering closer to the MORB end member. Aleutian intrusive samples overlap with the lava field, but, on average, plot to higher Sr/Y and La/Yb for a given δ^7 Li value. Neither intrusive samples nor lavas exhibit a correlation between δ^7 Li values and either Sr/Y or La/Yb. The sample with the highest δ^7 Li value has lower Sr/Y and La/Yb ratios than other intrusive samples, while the other two intrusive samples with δ^7 Li values > MORB either plot within the range of the other intrusions or show conflicting results (i.e., high La/Yb but not Sr/Y). Samples with δ^7 Li values < MORB fall within the trace element ratio range of the other samples.

Figures 2.8a and 2.8b show δ^7 Li values for Aleutian samples plotted against trace element ratios indicative of slab fluids: Li/Y and Cs/La. Global MORB values of White and Klein (2014) and Penniston-Dorland et al. (2017) and modeled slab fluid values of Singer et al. (2007) are included for reference. Trace element ratios of Aleutian lavas and intrusions cover roughly the same range of values between the two end member compositions. Both lava and intrusion data cluster closer to MORB values for Li/Y (Figure 2.8a), but span a continuum of values for Cs/La. δ^7 Li values of most lavas and intrusive samples plot within or below the MORB range, while three samples with less than ~56 wt.% SiO₂ have δ^7 Li values that fall above the MORB range and below the slab fluid end member. Neither intrusive samples nor lavas exhibit a correlation between δ^7 Li values and either Li/Y or Cs/La. With respect to samples with δ^7 Li values > MORB, Li/Y and Cs/La ratios seem to yield opposing results. For example, the intrusive sample with the highest δ^7 Li value also has Cs/La ratios higher than the other intrusive samples, but has the second lowest Li/Y. By contrast, another high δ^7 Li value intrusive sample has high Li/Y, but low Cs/La. Samples with δ^7 Li values < MORB fall within the range of the other Aleutian samples.



Figure 2.7. Plot of δ^7 Li versus a. Sr/Y and b. La/Yb. Global MORB Li isotope value from Penniston-Dorland et al. (2017); Trace element values from White and Klein (2014). Proposed slab melt from Kelemen et al. (2003). Sr, Y, La, and Yb data for Aleutian samples are from Kay et al. (1983); Kay et al. (1990); Kay and Kay (1994); Class et al. (2000); Yogodzinski et al. (2015); and Kay et al. (2019). Sample MOF53A (ADK-53) has a La/Yb ratio of 31 and therefore does not appear on Figure 2.7b. The δ^7 Li error bar for Aleutian samples is ±1.0‰.

5. Discussion

5.1 Previous studies of δ^7 Li values as a tracer of slab signatures

Previous studies have examined Li isotopes as a slab component tracer, though they vary in their success and sometimes yield conflicting results. Moriguti and Nakamura's (1998b) study of Li cycling in the Izu arc noted an across-arc trend between δ^7 Li and slab depth, which the authors attributed to the transfer of isotopically heavy Li from the subducting slab to the mantle. However, Moriguti et al. (2004) did not find evidence of a slab signature in data from the northeastern Japan arc, which is contiguous with the Izu arc.

Chan et al. (2002b) analyzed samples from the Guatemala, El Salvador, Nicaragua, and Costa Rica portions of the Central American Volcanic Arc (CAVA), and noted that only the Nicaraguan samples exhibit correlations between Li isotopes and slab fluid indicators such as B/La and Y/Li. Clift et al. (2005) significantly expanded data for the Costa Rican portion of the arc and found an inverse correlation between δ^7 Li and Li/Y, which was not previously observed. Additionally, modeling of δ^7 Li versus ϵ Nd suggested the presence of a slab component in Clift et al.'s data, however crustal assimilation is also required.

Some studies have yielded negative results, which they sought to explain by invoking mantle reaction processes. Tomascak et al. (2000) attributed a lack of correlation between δ^7 Li and B/Be in Panama arc samples to sequestration of slab-derived Li in the sub-arc mantle. Likewise, Tomascak et al. (2002) proposed removal of Li by mantle chromatography to explain a lack of correlation between δ^7 Li and trace element ratios in Kurile, Sunda, and Aleutian arc lavas. However, Plank (2014) noted that mantle chromatography fails to explain the



Figure 2.8. Plot of δ^7 Li versus a. Li/Y, b. Cs/La. Li isotope data for slab fluid from Tang et al. (2014); trace element concentrations for slab fluids from Singer et al. (2007). Global MORB Li isotope value from Penniston-Dorland et al. (2017); trace element values from White and Klein (2014). Y, La, and Cs concentrations for Aleutian samples are from Kay et al. (1983); Kay et al. (1990); Kay and Kay (1994); Class et al. (2000); Yogodzinski et al. (2015); and Kay et al. (2019). The δ^7 Li error bar for Aleutian samples is $\pm 1.0\%$.

enrichment of Li relative to Y in arc lavas compared to MORB (see Figure 2.8a of this paper and Figure 2.9 of Plank, 2014), which suggests that equilibration of these elements with the mantle does not occur. Rayliegh distillation modeling by Caciagli et al. (2011) was also used to argue against Tomascak et al.'s chromatography model, as preferential partitioning of ⁶Li into the mineral phase would produce isotopically heavy liquids, not the MORB-like δ^7 Li signatures seen in most arc lavas.

A final group of studies examining Li cycling in subduction zones have yielded more positive results. Leeman et al. (2004) and Magna et al. (2006a) both identified a slab component in data from different segments of the Cascadia arc. Leeman et al. (2004) noted that basalts from the southern Washington portion of the Cascadia arc exhibit a very slight positive correlation between δ^7 Li and Li/Y, while Magna et al. (2006a) observed an overall inverse correlation between δ^7 Li and distance from the trench in samples from the northern California portion of the Cascadia arc. Ultimately, both studies attributed δ^7 Li trends in their respective data sets to a slab fluid signature.

Brens et al. (2019) noted a lack of correlation between δ^7 Li values and sediment tracers in samples from the Tonga-Kermadec arc, but concluded that elevated Li/Y ratios required the presence of a sediment component. Modeling of δ^7 Li versus Y/Li suggested that mixing of 1-3% sediment with a mantle end member could explain their observations, with fluid scavenging of Li possibly inflating that estimate (Brens et al., 2019).

Tang et al. (2014) present the strongest evidence yet for the presence of slab-derived Li in their study of isotopically light Martinique lavas. The authors used a Monte Carlo simulation to create a two-component, δ^7 Li versus Y/Li mixing model which suggests their data can be reproduced by addition of ~2% subducted sediment to depleted mantle.

The Tang et al. (2014) study benefitted from the substantial difference in δ^7 Li values between the mantle and subducting sediment in the Lesser Antilles (the mean δ^7 Li value of sediment is -0.8 ± 1.5‰ for DSDP Site 543 and -1.3 ± 2.9‰ for DSDP Site 144; Tang et al., 2014). However, such a significant difference may not be necessary since some authors have successfully modelled a slab signature when the average δ^7 Li value of subducting sediment falls within the mantle range. A slab signature was noted in the Nicaragua arc (δ^7 Li = 5.6‰) by both Chan et al. (2002b) and Plank (2014); in the Cascadia arc (δ^7 Li = 2.2‰) by both Leeman et al. (2004) and Magna et al. (2006a); in the Tonga-Kermadec arc (δ^7 Li = 5.0‰) by Brens et al. (2019); and in the East Sunda data of Tomascak et al. (2002) by Plank (2014). This suggests that, even when Li isotopic signatures of a slab component are not drastically different from mantle values, Li isotopes, in combination with radiogenic isotope or trace element ratios, can still be used as a slab component tracer.

5.2 δ^7 Li values and an Aleutian slab signature

Many of the existing studies of Li in arcs rely on models that combine δ^7 Li values with trace element ratios, particularly Li/Y, to detect slab signatures (Chan et al., 2002b; Tomascak et al., 2002; Leeman et al., 2004; Clift et al., 2005; Magna et al., 2006a; Plank, 2014; Tang et al., 2014). While trace element ratios are viable tracers of slab components, their use can sometimes be problematic. The divergence of distribution coefficients in higher SiO₂ lavas (>56 wt.%), combined with potential magma mixing, crustal assimilation, and crystal fractionation in more evolved samples can impact the usefulness of trace element ratios. Given the prevalence of more evolved lavas in the Aleutian data set, trace element ratios can only be used to model a subset of the data. Within the remaining samples, trace element ratios do not always behave as expected. For instance, Ba/La, generally considered to track slab fluids, is strongly correlated with Th/La in Aleutian lavas (Kay and Kay, 1994; Kelemen et al., 2003; Schaen et al., 2016; Kay et al., 2019) setting the Aleutians apart from other arcs worldwide (Elliott, 2003). Ba is fluid mobile while Th is immobile, thus, if Ba/La was a proxy for slab fluids in Aleutian magmas, this correlation should not exist. However, Ba and Th are both incompatible during melting, thus, in the Aleutians, these elements are likely transported from the subducting slab into the mantle wedge via silicate melt, with or without slab fluids (Kelemen et al., 2003).

Trace element ratios applied to the Aleutian data also yield complicated and sometimes conflicting results. For instance, the intrusive samples show a general trend of increasing Th/Nd with increasing δ^7 Li values (R² = 0.65; Figure 2.6b), which could suggest a sediment melt influence on δ^7 Li values. A similar positive trend should also be seen between Th/La and δ^7 Li, yet the R² value for this pair is only 0.41. Another example is the conflicting results of Cs/La and Li/Y in samples with δ^7 Li values > MORB range. These complications suggest it may be useful to explore alternative proxies for deciphering slab components in the Aleutians, particularly for plutonic samples whose trace element ratios can be affected by mineral addition and removal.

Radiogenic isotopes can provide an alternative for slab signature modeling and have been successfully used in previous Aleutian studies. Kay et al. (1978) determined that a 2% sediment component could explain isotopic compositions of Aleutian volcanic samples based on mass balance calculations using Sr and Pb isotopes. Class et al. (2000) calculated the addition of up to 1.5% sediment fluid and up to 2.5% sediment melt to the mantle source of lavas from Umnak island, with sediment melt dominating Nd isotopic ratios, and sediment fluid dominating Pb isotopes. Jicha et al. (2004), using Sr, Nd, Pb, and Hf isotopes, focused on the role of sediment fluid contributions, and calculated a contribution of 0.2% to 5% to Aleutian lavas, depending on the volcanic center. Finally, Yogodzinski et al. (2010) conclude that a 2-3% sediment component is present in the mantle source of Aleutian lavas based on ε_{Hf} and ε_{Nd} . They argued that a sediment melt component is necessary to produce the elevated Nd/Hf ratios of Aleutian samples, but do not quantify what percentage of the sediment component in the model is sediment melt.

Aleutian intrusive samples show an overall relationship of increasing δ^7 Li values with increasing Th/Nd ratios (Figure 2.6b), suggesting that additional exploration into the presence of a sediment melt signature may be warranted. To further examine this possibility, one mantlesediment fluid mixing model, one mantle-sediment melt mixing model, and one mixing model that employs all three end members were calculated using the parameters in Table A2.2. These mixing models use Nd isotope ratios in combination with δ^7 Li values because 1) radiogenic isotopes do not have the compositional limitations of trace element ratios for evolved lavas and intrusions; and 2) Nd is the only isotopic system for which data exist for a majority of both lava and intrusive samples.

The Depleted Mantle-Sediment Melt mixing scenario extends between the depleted mantle end member and the sediment melt end member in Figure 2.9. The depleted mantle, which has been used for modelling in previous studies (e.g., Leeman et al., 2004; Tang et al., 2014; Brens et al., 2019), was chosen to represent an unmodified mantle end member with which to mix sediment components. Nd and Li concentrations for the depleted mantle are from Salters and Stracke (2004), and Nd isotope ratios are from Jicha et al. (2004; Table A2.2). The Li isotope value of the depleted mantle end member represents the average mantle value of

Penniston-Dorland et al. (2017). Nd and Li concentrations of the sediment melt end member were calculated using partition coefficients of Johnson and Plank (2000) and assume 5% melt in equilibrium with DSDP Hole 183 sediment. Li and Nd isotope ratios of the sediment melt end member are those reported for DSDP Hole 183 sediment by Chan et al. (2006) and Plank (2014), respectively (Table A2.2).



Figure 2.9. Depleted mantle-slab fluid mixing model for δ^7 Li versus ¹⁴³Nd/¹⁴⁴Nd. The + symbol on Depleted Mantle-Sediment Fluid and Modified Mantle-Sediment Fluid Mixing Scenarios indicates 1-3% sediment fluid component. The + symbol on Depleted Mantle-Sediment Melt mixing scenario indicates 1-5% sediment melt component. See Table A1.2 for values and associated references for the three mixing scenarios. The δ^7 Li error bar for Aleutian samples is $\pm 1.0\%$.

The Depleted Mantle-Sediment Fluid mixing scenario extends between the depleted mantle end member and the sediment fluid end member with the higher δ^7 Li value (Figure 2.9). This scenario uses the same depleted mantle end member as above, but instead mixes it with a sediment fluid end member (Table A2.2). Neodymium and Li concentrations of the sediment fluid end member were calculated using partition coefficients of Johnson and Plank (2000) and assume 5% fluid in equilibrium with DSDP Hole 183 sediment. The Nd isotope ratios of the sediment fluid end member are those reported for DSDP Hole 183 sediment by Plank (2014; Table A2.2). Previous studies adopted a range of Li isotopic compositions for sediment fluid, from ~10‰ in Moriguti and Nakamura (1998a) to 20‰ in Tang et al. (2014). A mid-range value of 15‰ provided the best solution for Aleutian data in this mixing scenario (Table A2.2).

The Modified Mantle-Sediment Fluid mixing scenario extends between a modified mantle end member and the sediment fluid end member with the lower δ^7 Li value (Figure 2.9). The modified mantle end member represents 3% sediment melt addition to the Li and Nd concentrations and isotopic values of the depleted mantle (Table A2.2). The Nd isotope ratios of the sediment fluid end member are those reported for DSDP Hole 183 sediment by Plank (2014), and the δ^7 Li value of sediment fluid is from Moriguti and Nakamura (1998a).

Two samples from our study meet the adakite geochemical criteria of Kelemen et al. (2003): a porphyritic diorite from the Hidden Bay pluton (HB7-16), and an 11.8 ± 0.3 Ma sample from a flow stratigraphically under the Moffett flows (MOF53A, also reported as ADK-53; see Jicha and Kay, 2018, for more information on this sample). This sample is the original 'adakite' from Kay (1978). However, we do not consider a subducting eclogite melt component for the Aleutian samples because recent work has discredited slab melting as the source of the adakite

geochemical signature. Instead, adakite-like signatures are attributed to subduction erosion and subsequent melting of the mafic Aleutian forearc (Kay, 2003; Jicha and Kay, 2018; Kay et al., 2019). The potential for mixing between a depleted mantle end member and a slab fluid end member that includes altered oceanic crust, such as the slab fluid from Singer et al. (2007) used in Figure 2.8, was explored in our modeling. However, the model proved to be a poor fit for the Aleutian data, in part because of the similar Nd isotope ratios between the altered oceanic crust and the depleted mantle. This suggests the inability to discern altered oceanic crustal components may be a disadvantage of the isotopic modelling employed in this study.

Only a few Aleutian samples fall along the Depleted Mantle-Sediment Fluid mixing scenario line, suggesting two-component mixing between depleted mantle and sediment fluid may not adequately explain the Aleutian data. Of particular issue are the lower than MORB-range of δ^7 Li values of several samples, which would require depleted mantle δ^7 Li values of ~2‰, which have not been observed (e.g., δ^7 Li values in unaltered peridotite xenoliths range from ~+2.5‰ to ~+4.9‰; Brooker et al., 2004; Seitz et al., 2004; Magna et al., 2006b; Jeffcoate et al., 2007; Magna et al., 2008; Gao et al., 2011; Pogge von Strandmann et al., 2011; Lai et al., 2015, with an average of 3.8 ± 0.7 , Penniston-Dorland et al., 2017). A more likely scenario may be the presence of a sediment melt component that can skew the δ^7 Li values of MORB-range samples to slightly lower values than if sediment fluid was the only slab influence (Figure 2.9). Thus, the majority of Aleutian samples may be explained by the addition of <1% sediment fluid to a mantle component that may have been modified by up to ~3% sediment melt (Figure 2.9). This result is consistent with the previous Aleutian isotope studies discussed above, and with models using δ^7 Li values and 206 Pb/²⁰⁴Pb ratios (Figure 42.2; Table A2.3).

The mixing models in Figure 2.9 suggest a sediment fluid component may be the dominant influence on most samples with δ^7 Li values greater than the MORB range, however, it does not explain the sample with the highest δ^7 Li value. This sample, a gabbro xenolith from Great Sitkin island with an unknown geologic context, also has low Li concentration (2.8 ppm) suggesting it may be best explained by diffusive loss of ⁶Li to the host lava. The models also does not explain the lava and intrusive samples with δ^7 Li values < MORB range, since the δ^7 Li values of sediment in DSDP Core 183 do not extend to low enough values (Chan et al., 2006). These samples plot within the range of the rest of the data with respect to trace element and radiogenic isotope ratios, suggesting their low δ^7 Li values do not result from source heterogeneity. The cause of these anomalously low δ^7 Li values is unknown at this time, though it is possible that the average δ^7 Li value of DSDP Core 183 is not representative of all sediments being subducted beneath the Aleutians and that regional variations may exist.

5.3 Implications for modeling a sediment signature using δ^7 Li values

Many studies have relied on spatial trends in δ^7 Li (Moriguti and Nakamura, 1998b; Moriguti et al., 2004; Magna et al., 2006a) or correlations between δ^7 Li values and slab component indicators (Tomascak et al., 2000; Chan et al., 2002b; Tomascak et al., 2002; Leeman et al., 2004; Tang et al., 2014) when evaluating the presence of a slab signature in arc lavas and intrusions. However, the results of this study suggest a slab signature may be present in Li isotope data, even when obvious trends between δ^7 Li values and other tracers are absent. Instead, mixing models combining δ^7 Li values with radiogenic isotopes or trace element ratios may be necessary to decipher the presence of slab signatures in arc lavas and intrusive samples (Moriguti and Nakamura, 1998b; Clift et al., 2005; Plank, 2014; Tang et al., 2014). This is also illustrated by the model of Plank (2014), which found a slab signature in the East Sunda data of Tomascak et al. (2002) after the original study came to a negative conclusion based on a lack of correlations between Li isotopes and trace element ratios.

Our study also suggests it may be necessary to use more than two slab components in mixing models to adequately explain some data sets. While some studies have demonstrated that two-component models explain some arc Li isotope data (e.g., Plank, 2014; Tang et al., 2014), a three component model incorporating both sediment melt and sediment-derived fluid is preferred for the Aleutian data. The inclusion of a melt component is in line with previous studies, which have also suggested a sediment melt component in the Aleutians (Class et al., 2000; Yogodzinski et al., 2010). The presence of sediment melt may partially offset the higher δ^7 Li values from sediment-derived fluid, particularly in arcs with lower sediment δ^7 Li values. Therefore, a sediment melt component may play a role in keeping many arc lava δ^7 Li values within the MORB range.

Finally, this study supports earlier studies that have shown that Li isotopes can be useful in settings where the δ^7 Li values of subducting sediments fall within the mantle range (Leeman et al., 2004; Clift et al., 2005; Magna et al., 2006a; Plank, 2014), particularly when used in conjunction with other isotopic systems. Of the arcs with published Li isotope data (Izu, Japan, Sunda, Lesser Antilles, Kurile, Guatemala, Costa Rica, El Salvador, Nicaragua, Panama, Cascadia, and the Aleutians), the majority have had slab signatures detected in the δ^7 Li data. While some of the seven arcs have sediment δ^7 Li values well above (Izu arc) and well below (Sunda, Lesser Antilles) the MORB range, sediment from the other arcs fall within the MORB

range (Aleutian, Cascadia, Nicaragua, Costa Rica). This has important implications for the usefulness of Li isotopes as a sediment tracer because 20 of the 30 arcs reported in Plank (2014) have average subducting sediment with MORB range δ^7 Li values. Thus, with appropriate modeling, Li isotopes could have widespread applicability as a tracer of sediment signatures, even in arcs where the δ^7 Li values of sediment do not vary drastically from the MORB range.

6. Conclusions

Li isotope values of Aleutian lavas and intrusions span the entirety of the MORB range, with three samples falling below the range and five falling above. The $\delta^7 Li$ values of Aleutian samples do not show the spatial variability observed in some other slab component tracers (e.g., B/La, B/Nb, B/Be, Cs/La, Pb/Ce; Singer et al., 2007) nor do they exhibit correlations with most of these tracers. However, modeling δ^7 Li values in combination with ¹⁴³Nd/¹⁴⁴Nd ratios suggests that most Aleutian lavas and intrusive samples that fall within or above the MORB δ^7 Li range may be explained by mixing <1-2% sediment fluid and up to $\sim3\%$ sediment melt with a depleted mantle source; estimates that are in line with previous studies using non-Li slab component tracers. The model also suggests that sediment fluid plays a larger role in samples with δ^7 Li values greater than the MORB range, while the presence of a sediment melt could skew the δ^{7} Li value of MORB-range Aleutian samples to slightly lower values than if sediment fluid was the only slab influence. Alcutian samples with δ^7 Li values less than the MORB range cannot be explained by the addition of slab components because none of the slab components have δ^7 Li values low enough, though it is possible that the δ^7 Li of subducting sediment varies beyond that observed in the single drill core that is available.

The results of this study indicate that a sediment signature may be present in Li isotope data, even when spatial trends and correlations with slab component indicators are not evident. Modeling may be required to decipher these signatures, and these models may need to accommodate both sediment-derived fluid and sediment melt in some arcs.

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CHAPTER 3: IMPACT OF WEATHERING ON THE MINERALOGY AND CHEMISTRY OF SOILS FROM SAN CRISTOBAL ISLAND, GALAPAGOS

1. Introduction

Chemical weathering of crustal silicate rocks plays a vital role in global processes such as oceanic nutrient fluxes and atmospheric CO₂ regulation (Misra and Froelich, 2012; Penniston-Dorland et al., 2017). Chemical weathering of basalt, in particular, is an important contributor to atmospheric CO₂ regulation. Despite representing only ~8% of exposed silicate rock (Gaillardet et al., 1999), basalt chemical weathering is responsible for 30-35% of global CO₂ consumption (Dessert et al., 2003). Thus, characterizing the complexities of basalt weathering can provide an important foundation for large scale research on some of Earth's systems. Economically, basalt weathering is important to study as extreme weathering forms laterites, which are important iron ores. Finally, progressive weathering of basalt results in elemental loss, which can impact soil fertility (Kronberg and Nesbitt, 1981).

The often-cited weathering order for silicates in basalt is glass \approx olivine > plagioclase \approx pyroxene > Fe-Ti oxide (e.g., Nesbitt and Wislon, 1992), however, variability in that weathering sequence has been documented (Eggleton et al., 1987, and references therein). Structure influences how readily minerals chemically weather, with those that have leachable cations connecting Si tetrahedra (e.g., olivine), being more prone to congruent dissolution than those with more bridging O bonding Si tetrahedra (e.g., pyroxene) (Chorover and Chadwick, 2001). Environmental factors can also play a role in how some minerals weather. For example, felspars can weather both congruently to form amorphous to poorly crystalline phases and incongruently

to form crystalline phases depending on environmental factors such as CO₂ concentrations and the presence of complexing ligands (Chorover and Chadwick, 2001). As these minerals break down, the elements released are either leached from the system or incorporated into secondary minerals, while increasing weathering intensity progressively removes cations from the system, impacting which secondary minerals can from. Ultimately, all of the silicate minerals in basalt are altered to a combination of clay minerals, Fe-oxide-hydroxide, and amorphous allophane (Eggleton et al., 1987).

Progressive weathering of basalt forms soils whose properties reflect a complicated interplay of amorphous and crystalline weathering products, organic material, and solutions that can change on a range of time scales. The availability of water to leach soil ions has a major influence on soil chemical properties and secondary mineral formation (Chadwick et al., 2003), by impacting factors such as intensity of cation leaching, mineral stability, and plant growth (Chorover and Chadwick, 2001). For example, when leaching is less intense and base cations remain, smectite can form, whereas more intense leaching leads to kaolinite formation instead (Chorover and Chadwick, 2001). However, while research has examined climatic influence on secondary mineral formation (e.g., Chadwick et al., 2003), knowledge gaps remain with respect to the influence of changing climate on mineralogical control of elemental behavior.

This research aims to improve the understanding of how the different climate zones on San Cristóbal island, Galapagos, impact weathering of the underlying basalt and the resulting mineralogy and soil chemistry. The Galapagos islands were established as a UNESCO World Heritage site in 1978, and have since been identified as one of the world's 100 most irreplaceable sites (Le Saout et al., 2013). However, increasing immigration and tourism on the islands are posing ever greater threats to the delicate ecosystems of the archipelago (González et al., 2008).

To aid conservation efforts, high priority questions whose answer would be of significant benefit to conservation and sustainability efforts have been identified. How soils vary across the Galapagos islands has been identified as one of those questions in need of answering (Izurieta et al., 2018).

To date, research into Galapagos soils has focused heavily on Santa Cruz island, while San Cristobal soils have been less thoroughly examined (Stoops, 2014). San Cristobal is older than Santa Cruz and soils have been characterized as Alfisols instead of the Mollisols and Inceptisols noted for Santa Cruz (Adelinet et al., 2008; Stoops, 2014). Thus, research on Santa Cruz is not necessarily applicable to San Cristobal. Additionally, San Cristóbal has the longest history of agriculture among the Galapagos Islands (Stoops, 2014) with agriculture occupying 17.7% of the islands total area (Lasso and Espinosa, 2018). The most detailed published studies to date have been by Adelinet et al. (2008), who examined soil mineralogy and hydrodynamic properties, and a more vegetation-focused soil phytolith study by Astudillo (2018). Additionally, Franz (1980) provided and overview of soil types in some areas of San Cristobal, while Lasso and Espinosa (2018) summarized some findings in a Spanish-language publication by Wicknell (1997). Since sustainable agriculture is an important topic in the Galapagos, an improved understanding of the impact of weathering on soil chemistry could also help inform these practices in accordance with the Galapagos National Park's management plan.

2. Geologic Setting and Samples

San Cristobal Island, located on the easternmost side of the Galapagos archipelago (Figure 3.1a) where the Nazca plate has moved off of the hotspot (Geist et al., 2008), provides an ideal location to study the impact of climate on basalt weathering. Morphologically, San


Figure 3.1 a. Map of climate zones on the Galapagos islands after Huttel (2008) and b. San Cristobal island with LiDAR base to show topography. Location of San Cristobal island shown in red box. Climate zones from part a are overlain on LiDAR base with 70% transparency. Black lines and corresponding numbers denote age distribution of lava flows as determined using flow morphology and paleomagnetism by Geist et al. (1986). Ages range from Group 1 lavas, inferred to be the oldest with K-Ar age of 2.32 Ma, to Group 6 lavas, inferred to be the youngest based on plant development and surface weathering. See Figure 1 of Geist et al. (1986) for more information. Lavas to be sampled in this study are mostly Group 3 lavas with site in the Group 2 lavas.

0 1 2

HH

4

8

Miles

Cristobal is composed of two separate volcanoes, but geochemical similarities in the lavas suggest they result from the same volcanic plumbing system (Geist et al., 2008). An extinct shield volcano forms the southwestern portion of San Cristobal and provides the island's topographic high (Figure 3.1b). In contrast, the low elevations to the northeast are dominated by a newer series of fissure eruptions (Geist et al., 1986). Compositionally, the island is almost entirely basalt, which ranges in age from 2.33 ± 0.13 Ma to an estimated <1 ka (Geist et al., 1986). Soils are best developed on the windward (southeast) side of the shield volcano (Adelinet et al., 2008) where most lavas have been determined to be of Brunhes age by magnetic polarity measurements (Group 3 in Figure 3.1b) with two K-Ar ages measured at 0.66 Ma and 0.89 Ma (Geist et al., 1986). The transition between the normal polarity Brunhes and the reverse polarity Matuyama occurred ~0.7 Ma (Cox, 1971). Thus, the 0.89 Ma date suggests some Group 3 lavas are more consistent with Group 2 lavas, which formed between ~ 1 Ma and ~ 0.7 Ma during Matuyama (Cox, 1971). Group 2 lavas are concentrated within the study area at lower elevations (<~150 to ~180 m) on the southwestern side of the shield volcano (Figure 3.1b; Geist et al., 1986).

The trade winds and ocean currents that control the Galapagos climate are themselves controlled by the influence of the Inter Tropical Convergence Zone (ITCZ) and the El Niño Southern Oscillation (ENSO; Trueman and D'Ozouville, 2010). The result is a climate that is colder and drier than is generally found at the equator (Adelinet et al., 2008). The ITCZ migrates between 10°N during the northern hemisphere summer and 3°N during the northern hemisphere winter resulting in a hot season (January to May), during which the substantial rain can fall on lowlands, and a cold season (June to December, during which a temperature inversion causes abundant stratus clouds that increase moisture in the highlands (Trueman and D'Ozouville, 2010;

Lasso and Espinosa, 2018). The presence of these stratus clouds has caused elevation-related climate zonation up the steep topography of the shield volcano (Figure 3.2; Trueman and D'Ozouville, 2010). An arid zone is present at the coast, which receives <400 mm/yr of precipitation (Huttel, 1986). Next, a dry zone is present in the lowlands, which receives < 800 mm/yr of precipitation (Huttel, 1986). A transition zone is located mid-way up the side of the shield volcano. This zone receives 800 to 1100 mm/yr of precipitation (Huttel, 1986) and represents the soft boundary between dry and humid zones (Trueman and D'Ozouville, 2010). Finally, the humid zone is located at higher elevations on the island and receives annual precipitation up to 1,500-2,000 mm/yr (Huttel, 1986; Adelinet et al., 2008). While these climate zones are present on all sides of the shield volcano, the north-facing leeward side is drier than the southern-facing windward side (Huttel, 1986) in part because the former only receives rain from heavy storms that occur during the hot season (Adelinet et al., 2008).

Thus, San Cristobal is an ideal place to study basalt weathering and the resulting soils because of the relatively uniform age and composition of the shield volcano, combined with the different climate zones at different altitudes. This allows for the source material to be held relatively constant while examining the effect of differences in rainfall and, by extension, degree of weathering. Additionally, the presence of abundant secondary mineral formation due to basalt weathering has also been documented in Galapagos basalts (Adelinet et al., 2008).

Basalt and/or saprolite and soil samples were collected from 6 sites representing the range of climate zones on the island (Figure 3.2). Three of the sites (Cerro Colorado, San Joaquin 2 and San Joaquin 1) sampled exposed profiles, such as road cuts or abandoned quarry faces. For these profiles, a shovel, trowel, and hand axe were used to clean off surficial material and expose new soil, saprolite, and/or rock for sampling. The Cerro Colorado site (Figure 3.2),



Figure 3.2. Map of study area on San Cristobal Island showing climate zones and sample locations.

located in an abandoned quarry in the dry zone at ~120 m elevation, sampled a 160 cm-thick profile which consisted of a thin (<20 cm) soil horizon underlain by cohesive rock. For the top 20 cm, samples were collected every 10 cm, starting at the surface, to sample the thin layer of loose material above the cohesive rock which begins ~20 cm depth. From 20 cm to 160 cm, samples were collected every 20 cm due to visual homogeneity of the profile and difficulty of collecting samples from the well-indurated rock. Photographs of the Cerro Colorado site from before and after sampling are shown in Figure 3.3a. A fresh sample was not possible to collect at the Cerro Colorado site given the nature of the quarry, so a sample was collected from the giant tortoise breeding center across the street. A second sample was collected from a relatively large (~2 ft length) boulder from a dry creek bed near Puerto Chino beach approximately 1 km away.

sample from the giant tortoise breeding center did not contain fresh material. The Puerto Chino sample did contain fresh rock, and thus was analyzed as a potential representative rock composition for Cerro Colorado samples.

A pit was dug for sampling at the Socavòn site, which is located in the dry to transition zone at ~180 m elevation (Figure 3.2). Socavòn contained a thicker soil horizon (~40 cm) underlain by saprolite. Sample locations were scored into the pit wall every 10 cm from the top down, including a saprolite sample at the bottom of the pit (46 cm). Samples were then collected from the bottom of the pit up to prevent contamination of lower samples by debris falling from the upper portion of the profile during sampling. Since digging the pit contaminated the surface with soil from deeper in the hole, a 0 cm sample was collected a few feet away in an uncontaminated area. Finally, a corresponding rock sample was collected from an outcrop at that site. Photographs of the Socavòn site from before and after sampling are shown in Figure 3.3b.

The San Joaquin 2 site (Figure 3.2), located in a road cut at ~470 m elevation in the humid zone, was the longest profile collected at 170 cm. The San Joaquin 2 site was composed of soil for the top ~55 cm, which was underlain by saprolite. Soil and saprolite samples were collected every 10 cm, and a corresponding rock sample was collected from an outcrop adjacent to the soil profile in the road cut. Photographs of the San Joaquin 2 site from before and after sampling are shown in Figure 3.3c.

A 120-cm profile was sampled from the San Joaquin 1 site at ~540 m elevation in the humid zone (Figure 3.2), which was composed of ~90 cm-thick soil underlain by saprolite. Soil and saprolite samples were collected every 10 cm starting at the surface. Photographs of the San Joaquin 1 site from before and after sampling are shown in Figure 3.3d. A corresponding rock



Figure 3.3. Before and after sampling photographs of a. Cerro Colorado and b. Socavòn profiles. Debris from sampling fell into the hole and obscured view of 46 cm sample in Socavòn after photograph. See text for details.



Figure 3.3, continued. Before and after sampling photographs of c. San Joaquin 2 and d. San Joaquin 1 profiles. See text for details.

sample was collected from the nearest accessible outcrop, located ~100 m away. Finally, a surficial soil grab sample and corresponding rock sample were collected from a site on the rim of El Junco lake at ~670 m elevation in the humid zone (Figure 3.2). All samples were brought back to the Plasma Mass Spectrometry laboratory in the Department of Geological Sciences at UNC Chapel Hill for preparation and analysis.

3. Methods

Soil and saprolite samples were hand carried to the University of North Carolina at Chapel Hill and baked at 200°C for 4 minutes according to United States Department of Agriculture's Animal and Plant Health Inspection Service permit requirements. All subsequent sample preparation and elemental concentration analyses were conducted at the University of North Carolina at Chapel Hill. Soil samples were then ground using an agate mortar and pestle to facilitate more rapid digestion. More friable saprolite samples were powdered using an agate mortar and pestle while more indurated samples were powdered using a shatterbox. Weathered areas were removed from rock samples using a rock saw, then samples were cleaned using a sonicator and Milli-Q water, dried in a drying oven, and powdered using a shatterbox.

Powdered soil, saprolite, and rock samples were dissolved for elemental analysis according to a protocol modified from Chen et al. (2017). Approximately one hundred milligrams of each sample were weighed on weighing paper then transferred to a sealable 50 ml Teflon beaker. Three milliliters of H₂O₂ was immediately added to sample to oxidize organics and prevent loss of sample. The lid was placed on each beaker tight enough to prevent loss of sample during the initial oxidation reaction, but loose enough to allow built up volatiles to escape to prevent over pressurization. When vigorous initial reaction had subsided, lids were tightened

fully, and beakers were placed on at hotplate at 60°C overnight. The next day, the beaker lids were removed, and the samples were dried down at 50°C to prevent loss of sample due to splattering. Once H₂O₂ was evaporated, 3 ml of Aqua Regia and 0.5 ml of concentrated HF were added to the beakers, which were then recapped and placed on a 180 °C hotplate in a fume hood until sample dissolution was complete (usually 48 hours minimum). Sonicating was used as needed to facilitate dissolution in more difficult to dissolve samples. Beaker lids were then removed, and the beakers were dried down at 130 °C. Next, samples were fluxed on at 180 °C for 24 hours with intermittent sonication to facilitate dissolution of fluoride crystals. When dissolution was complete, samples were dried down at 130 °C then re-dissolved in 2 ml of concentrated HCl. Eight milliliters of Milli-Q water were then added to beaker to create a master solution from which to dilute aliquots for elemental analysis with an AgilentTM 7900 Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS). Q-ICP-MS analyses were evaluated using the BHVO-2 and SBC-1 standards, with analysis values, averages, uncertainties (2 standard deviation), and accuracy reported for both standards in Tables A3.1a and b and A3.2a and b.

Aliquots of select powdered soil, saprolite, and rock samples were also analyzed using X-Ray Diffraction (XRD) at the Chapel Hill Analytical and Nanofabrication Lab (CHANL) at the University of North Carolina at Chapel Hill. Diffraction patterns were collected on randomly oriented powder samples using the Rigaku SmartLab theta-theta diffractometer using CuK α radiation (40kV, 44mA) with Bragg-Brentano focusing and a K beta filter. Scans were conducted from 5° to 80° with a scan rate of 1° 20/minute, and quantitative mineralogical percentages were obtained using the Whole Powder Pattern Fitting function of the Rietveld Analysis, which is

built into the Rigaku PDXL software. Percentages given represent percentage of crystalline phases since the program does not quantify amorphous phases.

Nd isotope data were collected on select soil, saprolite, and rock powders from the Cerro Colorado, Puerto Chino, Socavòn and San Joaquin 2 sites at State Key Laboratory of Isotope Geochemistry at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Isotope separation was conducted using the two-column protocol of Ma et al. (2013). The first column, used to separate Rare Earth Elements (REE), was loaded with 1 g strong cation resin, which was then washed with 6 M HCl and Milli-Q water and conditioned with 2.5 M HCl. Next the 1 ml of sample was loaded, and the column was washed with 15 ml of 2.5 M HCl. Then the sample was collected using 15 ml of 6 M HCl. The REE eluate was dried on a hot plate then redissolved in 0.2 ml of 0.25 M HCl for Nd separation in column 2. The second column, which separated Nd from other REE, was loaded with 1 g Ln Spec resin, washed with 6 M HCl and Milli-Q water and pre-conditioned with 0.25 M HCl. The sample (0.2 mL) was loaded into the column, which was then washed with 10 ml of 0.25 M HCl. Finally, Nd was collected with 14 ml 0.25 M HCl and the column was washed with 6 ml of 6 M HCl to remove Sm. The resulting sample solutions were run using a Nu Plasma 1700 multi-collector-inductively coupled plasmamass spectrometer (MC-ICP-MS). Nd mass bias was corrected using sample-standard bracketing mode, and triplicate analysis of the JNDi Nd standard during the run yielded ¹⁴³Nd/¹⁴⁴Nd values 0.512110, 0.512110, and 0.512084 with an average ¹⁴³Nd/¹⁴⁴Nd value of 0.512101. GeoReM gives a compiled 143 Nd/ 144 Nd value of 0.512115, with a range of 0.51109 – 0.51295 based on 583 values (Jochum et al., 2005). Nd isotope analysis internal precision is about 1×10^{-5} (2 standard deviations; Ma et al., 2013).

Sr isotope analysis was conducted on select soil, saprolite, and rock powders from the Cerro Colorado, Puerto Chino, Socavòn and San Joaquin 2 sites at State Key Laboratory of Isotope Geochemistry at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Sr isotope separation followed the procedure of Zhu et al. (2018) wherein a column loaded with 0.25 ml Sr Spec resin was pre-conditioned with 3 N HNO₃. Next, a dissolved sample aliquot containing ~800 ng Sr was loaded into the column and eluted by 6.5 ml 3 N HNO₃. Finally, Sr was collected by 3 ml of 0.05 N HNO₃. Sr mass bias was corrected using 86 Sr/ 88 Sr = 0.1194, and repeat analysis of the SRM987 and BHVO-2 standards yielded average results of 87 Sr/ 86 Sr = 0.710252 and 0.703455, respectively. GeoRem gives and a range of 0.703404 – 0.7037 (128 values) for BHVO-2 (Jochum et al., 2005). The NIST certificate gives an 87 Sr/ 86 Sr ratio of 0.71034 ± 0.00026 for SRM987 (National Institute of Standards and Technology, 2007). Long-term reproducibility is ±0.000012 (2 standard deviations; Zhu et al., 2018).

4. Results

4.1 X-Ray Diffraction

XRD analysis indicates that dry zone Cerro Colorado samples are mainly composed of primary igneous minerals, with anorthite composing ~63% to ~81%, forsterite making up ~7% to ~22%, and augite composing ~7% to ~19% (Table 3.1). The only alteration mineral present is ferrihydrite which ranges from ~1% to ~9%. However, ferrihydrite is often poorly crystalline, making it difficult to detect with an XRD. Thus, these ferrihydrite percentages may be significantly underestimated. Additionally <1% cristobalite was indicated for the 160 cm sample, however, this may be an artifact caused by peak interference (Nelson et al., 2017). Moreover, the presence or absence of smectites could not be confidently determined with the Rigaku SmartLab

Sample	Depth (cm)	Sample Type	Forsterite	Anorthite	Augite	Ilmenite
Cerro Colora	ado, Dry Zone					
CC-0	0	Soil	21	66	11	-
CC-10	10	Soil	12	81	5	-
CC-20	20	Rock	7	76	16	-
CC-40	40	Rock	20	63	10	-
CC-80	80	Rock	13	66	19	-
CC-120	120	Rock	19	73	7	-
CC-160	160	Rock	22	68	9	-
Puerto Chino	o, Dry Zone					
PC-R1	0	Fresh Rock	6	76	18	-
Socavòn, Dr	y to Transition	Zone				
SV-0	0	Soil	-	-	-	-
SV-10	10	Soil	-	-	-	-
SV-20	20	Soil	-	-	-	-
SV-30	30	Soil	-	-	-	-
SV-40	40	Soil	-	-	-	-
SV-46	46	Saprolite	-	-	-	_
SV-R1	0	Fresh Rock	4	69	27	-
San Joaquin	2, Transition to	Humid Zone				
SJ2-0	0	Soil	5	29	20	_
SJ2-10	10	Soil	2	33	21	_
SJ2-30	30	Soil	-	31	15	-
SJ2-50	50	Soil	3	28	20	_
SJ2-70	70	Saprolite	11	28	18	_
SJ2-90	90	Saprolite	11	20	20	-
SJ2-110	110	Saprolite	4	33	23	-
SJ2-130	130	Saprolite	8	40	38	-
SI2-140	140	Saprolite	<1	35	17	_
SI2-150	150	Saprolite	-	21	17	_
SJ2-170	170	Saprolite	2	26	36	_
SI2.P2	0	Fresh Rock	10	53	37	

Table 3.1a. Primary Igneous Mineral Percentages from XRD

Sample	Depth (cm)	Sample Type	Forsterite	Anorthite	Augite	Ilmenite	
San Joaquin 1, Humid Zone							
SJ1-0	0	Soil	-	-	-	-	
SJ1-10	10	Soil	-	-	-	-	
SJ1-20	20	Soil	-	-	-	-	
SJ1-30	30	Soil	-	-	-	-	
SJ1-50	50	Soil	-	-	-	-	
SJ1-70	70	Soil	-	-	-	-	
SJ1-90	90	Soil	-	-	-	-	
SJ1-100	100	Saprolite	-	-	-	-	
SJ1-110	110	Saprolite	-	-	-	-	
SJ1-120	120	Saprolite	-	-	-	-	
SJ1-R1	0	Fresh Rock	6	79	9	7	
El Junco, Humid Zone							
E J-0	0	Soil	-	-	-	-	
EJ-R1	0	Fresh Rock	14	62	23	-	

Table 3.1a. Primary Igneous Mineral Percentages from XRD, Continued

since the sample holder interferes with analyses at angles below $\sim 8^{\circ}$, causing an important smectite peak to be missed.

XRD analysis of dry to transition zone Socavon samples indicates that all primary igneous minerals have been altered to clay minerals and Fe oxides and oxyhydroxides. Kaolinite and halloysite are the clay minerals detected by XRD in the Socavon samples, representing between 45% and 58% of the crystalline phases (Table 3.1a and b). Goethite (~16% to ~45%), and hematite (~1% to ~5%) make up the iron-bearing crystalline phases (Table 3.1b). Additionally, between ~18% and ~23% cristobalite is also present in the top 30 cm of the profile.

Sample	Ferrihydrite	Kaolin Minerals	Goethite	Hematite	Gibbsite	Cristobalite			
Cerro Colorado, Dry Zone									
CC-0	1	-	-	-		-			
CC-10	1	-	-	-	-	-			
CC-20	1	-	-	-	-	-			
CC-40	7	-	-	-	-	-			
CC-80	9	-	-	-	-	-			
CC-120	1	-	-	-	-	-			
CC-160	1	-	-	-	-	<1			
Duarta Chi	no Dru								
Zone	lio, Diy								
PC-R1	-	-	-	-	-	-			
Socavòn, I	Dry to Tranisiti	on Zone							
SV-0		51	28	3	_	18			
SV-10	-	45	30	2	-	18			
SV-20	-	43	16	15	-	23			
SV-20	-	55	23	1	_	21			
SV-40	-	58	38	4	_	-			
SV-46	-	48	45	7	_	_			
SV-R1	-	-	-	-	-	-			
San Joaqui	n 2, Transition	to Humid Zone							
SJ2-0	-	27	16	4	-	-			
SJ2-10	-	21	21	3	-	-			
SJ2-30	-	21	23	11	-	-			
SJ2-50	-	36	8	5	-	-			
SJ2-70	-	19	21	2	-	-			
SJ2-90	-	26	21	2	-	-			
SJ2-110	-	15	23	2	-	-			
SJ2-130	-	4	3	7	-	-			
SJ2-140	-	3	41	3	-	-			
SJ2-150	-	9	46	6	- 1	-			
SJ2-170	-	12	21	3	- 1	-			
SJ2-R2	-	-	-	-	-3	-			

Table 3.1b. Alteration Mineral Percentages from XRD.

Sample	Ferrihydrite	Kaolin Minerals	Goethite	Hematite	Gibbsite	Cristobalite
San Joaqu	in 1, Humid Z	Zone				
SJ1-0	-	27	52	6	15	-
SJ1-10	-	44	37	6	14	-
SJ1-20	-	44	36	5	15	-
SJ1-30	-	56	29	5	10	-
SJ1-50	-	34	44	8	14	-
SJ1-70	-	42	<1	23	34	-
SJ1-90	-	10	62	4	24	
SJ1-100	-	24	21	1	54	-
SJ1-110	-	23	12	5	60	-
SJ1-120	-	7	44	<1	49	-
SJ1-R1	-	-	-	-	-	-
El Junco,	Humid					
Zone						
EJ-0	-	6	51	12	31	-
EJ-R1	-	-	-	-	-	-

Table 3.1b. Alteration Mineral Percentages from XRD, Continued

Three sample sites are located in the area mapped as the humid zone. San Joaquin 2 samples contain a mixture of primary and secondary minerals in all samples (Table 3.1a and b). Anorthite comprises between ~1% and ~40%, augite makes up ~15% to ~38%, and forsterite ranges from ~0% to ~11% (Table 3.1a). Kaolinite and halloysite are the main clay minerals, collectively comprising from ~3% to ~36% of crystalline phases. The Fe-bearing crystalline phases are goethite, which ranges from ~3% to ~46% and hematite, which comprises between ~2% and ~11%; Table 3.1b). San Joaquin 1 and El Junco samples do not contain primary igneous minerals (Table 3.1a). Clay minerals in the San Joaquin 1 profile are composed of kaolinite and halloysite, which combined range from ~7% to ~56%, and gibbsite, which makes up between ~10% and ~60% of crystalline phases. The oxide and oxyhydroxide phases are

goethite which ranges from ~<1% to ~62%, and hematite which makes up ~<1% to ~24% (Table 3.1b). Finally, the El Junco soil sample is composed entirely of kaolinite and halloysite (~6%), gibbsite (~31%), goethite (~51%), and hematite (~12%).

4.2 Chemical Indices of Weathering

Chemical Index of Alteration (CIA) values were calculated for San Cristobal samples using major element data in Table 3.2. CIA is a weathering index that primarily reflects feldspar dissolution and the resulting loss of mobile CaO, Na₂O, and K₂O relative to Al₂O₃, latter of which is presumed to be immobile due to its incorporation into pedogenetic clay minerals (Babechuk et al., 2014). CIA is calculated as the molar ratios of

[Al₂O₃/(Al₂O₃+CaO*+Na₂O+K₂O)]x100, with CaO* representing the CaO in silicate phases after the contribution form carbonates and apatite has been removed (Nesbitt and Young, 1982). Idealized montmorillonites and illite have CIA values between 75 and 85, while idealized kaolinite plots close to 100 (Nesbitt and Young, 1982). Due to the low concentration of CaO in the samples and the lack of evidence for carbonates or apatite in the XRD data, we do not make the CaO* correction for our CIA and MIA calculations. The fresh basalt CIA range is 30 to 45 (Nesbitt and Young, 1982).

Rock samples from Puerto Chino (CIA = 45), Socavòn (CIA = 45), San Joaquin 1 (CIA=45), and El Junco (CIA= 44) plot at the upper end of this range, with the San Joaquin 2 rock plotting slightly above (CIA = 46; Figure 3.4). XRD analysis does not indicate the presence of alteration minerals, but it does suggest anorthite proportions from ~53% to ~79% (Table 3.1a and b). Unaltered anorthite has a CIA value of 50 (Nesbitt and Young, 1982), thus the anorthite

Sample	Depth (cm)	Sample	TiO ₂	Al_2O_3	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5
Cerro Colo	rado Dry	Zone									<u> </u>
	rado, Dry	Zone									
CC-0	0	Soil	1.32	16.17	8.07	0.15	8.03	6.11	2.33	0.95	0.26
CC-10	10	Soil	1.32	16.08	7.63	0.13	6.58	5.37	1.99	0.93	0.23
CC-20	20	Rock	1.52	18.99	9.13	0.17	7.59	6.77	2.66	1.15	0.24
CC-40	40	Rock	1.21	15.33	7.34	0.15	8.90	5.79	2.51	0.94	0.23
CC-60	60	Rock	1.27	15.58	7.86	0.15	8.62	6.21	2.48	0.98	0.24
CC-80	80	Rock	1.23	15.90	7.18	0.15	8.06	6.01	2.65	1.04	0.23
CC-100	100	Rock	1.23	16.11	7.08	0.17	7.42	6.00	2.74	1.05	0.23
CC-120	120	Rock	1.21	16.00	7.29	0.15	8.09	6.24	2.80	1.06	0.24
CC-140	140	Rock	1.33	15.84	8.31	0.16	7.92	6.63	2.68	1.08	0.27
CC-160	160	Rock	1.25	15.42	7.71	0.16	9.23	6.21	2.68	0.97	0.24
Puerto Chin	no, Dry Z	one									
PC-R1	0	Fresh Rock	1.10	18.19	9.05	0.19	8.92	9.98	2.43	0.13	0.10
San Joaqui	n 2, Trans	ition to Hum	id Zo	ne							
SJ2-0	0	Soil	1.88	20.62	13.26	0.22	8.38	3.35	0.80	0.42	0.17
SJ2-10	10	Soil	1.81	21.44	11.13	0.20	6.77	3.39	0.85	0.32	0.12
SJ2-20	20	Soil	1.96	21.48	12.82	0.23	4.88	3.84	1.01	0.47	0.12
SJ2-30	30	Soil	1.77	19.95	11.19	0.16	2.90	1.78	0.40	0.22	0.06
SJ2-40	40	Soil	1.87	20.82	10.93	0.21	5.62	4.21	1.19	0.39	0.19
SJ2-50	50	Soil	1.85	22.69	11.54	0.20	4.49	3.09	0.87	0.37	0.08
SJ2-60	60	Saprolite	1.91	20.25	11.81	0.20	8.49	4.41	0.94	0.36	0.12
SJ2-70	70	Saprolite	1.76	19.51	11.01	0.18	7.84	3.53	0.85	0.34	0.06
SJ2-80	80	Saprolite	1.82	19.38	10.84	0.20	9.04	4.30	1.08	0.37	0.16
SJ2-90	90	Saprolite	1.80	21.39	11.48	0.23	8.34	2.95	0.69	0.25	0.02
SJ2-100	100	Saprolite	1.38	17.01	9.17	0.19	9.02	3.57	0.90	0.32	0.09
SJ2-110	110	Saprolite	1.92	20.57	12.08	0.21	9.92	4.66	1.13	0.38	0.10
SJ2-120	120	Saprolite	1.76	20.02	10.80	0.26	9.60	3.98	0.98	0.32	0.09
SJ2-130	130	Saprolite	1.88	20.65	11.67	0.25	8.76	4.14	1.06	0.38	0.15
SJ1-140	140	Saprolite	1.94	23.36	11.20	0.16	2.45	1.04	0.20	0.10	0.02
SJ2-150	150	Saprolite	1.94	24.26	11.32	0.20	2.84	2.27	0.57	0.28	0.02
SJ2-160	160	Saprolite	1.94	21.11	11.41	0.24	6.52	4.62	1.19	0.45	0.20
SJ2-170	170	Saprolite	1.87	20.48	11.44	0.22	6.51	3.98	0.94	0.38	0.18
SJ2-R2	0	Fresh Rock	1.56	16.46	9.37	0.17	11.38	8.04	2.36	0.52	0.24

 Table 3.2. Major Element Concentrations in Oxide Weight Percent

Sample	Depth (cm)	Sample Type	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
San Joaquin 1, Humid Zone											
SJ1-0	0	Soil	3.96	27.44	21.01	0.07	0.53	0.22	0.04	0.09	0.86
SJ1-10	10	Soil	3.73	27.32	19.79	0.07	0.53	0.20	0.04	0.08	0.78
SJ1-20	20	Soil	3.99	31.21	22.29	0.08	0.49	0.28	0.03	0.08	0.85
SJ1-30	30	Soil	3.47	27.73	19.53	0.08	0.46	0.06	0.03	0.07	0.68
SJ1-40	40	Soil	3.42	29.15	18.44	0.09	0.64	0.43	0.03	0.06	0.65
SJ1-50	50	Soil	3.09	28.78	17.19	0.11	0.78	0.28	0.02	0.05	0.63
SJ1-60	60	Soil	2.82	31.12	15.11	0.14	1.02	0.06	0.03	0.02	0.56
SJ1-70	70	Soil	2.39	26.66	13.30	0.14	1.10	0.07	0.03	0.01	0.57
SJ1-80	80	Soil	2.94	32.27	15.24	0.15	1.80	0.09	0.05	0.02	0.72
SJ1-90	90	Soil	3.11	32.91	16.76	0.15	1.86	0.19	0.03	0.01	0.81
SJ1-100	100	Saprolite	2.17	33.80	11.27	0.21	1.44	0.08	0.04	0.01	0.92
SJ1-110	110	Saprolite	1.85	34.64	10.16	0.10	1.12	0.05	0.03	0.01	0.71
SJ1-120	120	Saprolite	2.24	42.45	11.98	0.16	0.94	0.07	0.03	0.01	1.00
SJ1-R1	0	Fresh Rock	1.38	16.86	7.69	0.16	6.57	6.77	4.12	1.35	0.28
Socavòn, D	rv to Tra	nsition Zone									
SV 0	0	Soil	268	21.00	15 51	0.25	0.71	0 50	0.10	0.16	0.24
SV-0	10	Soil	2.00	21.00	13.51	0.23	0.71	0.39	0.10	0.10	0.24
SV-10	20	Soil	2.75	23.30	14.00	0.24	0.67	0.34	0.10	0.13	0.10
SV-20	30	Soil	2.54	27.29	13.15	0.21	0.62	0.29	0.09	0.12	0.14
SV-40	40	Soil	2.20	20.43	14.07	0.22	0.01	0.22	0.11	0.11	0.12
SV-46	46	Saprolite	2.24	26.75	14.07	0.17	1 42	0.19	0.15	0.00	0.09
SV-R1	0	Fresh Rock	1.45	16.80	8 81	0.17	10.38	8 69	2 75	0.60	0.08
5.4-1(1	0	I TUSH KUUK	1.45	10.00	0.01	0.17	10.50	0.09	2.15	0.00	0.23
El Junco, H	lumid Zoi	ne									
EJ-0	0	Soil	4.37	37.01	26.06	0.17	2.43	1.31	0.23	0.21	1.30
EJ-R1	0	Fresh Rock	1.41	16.11	8.86	0.17	11.62	8.82	2.53	0.54	0.20

Table 3.2. Major Element Concentrations in Oxide Weight Percent

content of the rocks may be inflating the CIA value. Two San Cristobal basalts from White et al. (1993) have CIA values of 39 and 40. XRD data are not available for these samples, but CIPW norms suggest significantly lower proportions of anorthite (33.00 and 36.25).

CIA values for the Cerro Colorado site range from 47 near the bottom of the profile to 53 near the top of the profile (Figure 3.4). The Cerro Colorado samples have high plagioclase values (up to ~81%), which may be inflating CIA values, however, the presence of ferrihydrite in the XRD data confirms incipient alteration is occurring. Meanwhile dry to transition zone Socavòn soil and saprolite samples have CIA values ranging from 94 at the surface to 98 near the bottom of the profile (Figure 3.4).



Figure 3.4. CIA versus depth for San Cristobal samples. See text for details.

For the humid zone sites, San Joaquin 2 soil and saprolite samples display a jagged pattern encompassing a wide range of CIA values (66 to 91), with the majority of samples exhibiting CIA values from 66 to ~75 (Figure 3.4). Samples collected at 30 cm (CIA = 83), 140 cm (CIA = 91,) and 150 cm (CIA = 82) displaying noticeably higher values than the other San

Joaquin 2 samples (Figure 3.4). San Joaquin 1 and El Junco CIA values of \geq 97 and 93, respectively. However, CIA values of Socavòn, San Joaquin 1, and El Junco samples should be treated cautiously since the weathering index does not adequately quantify the behavior of elements at high degrees of alteration (Babechuk et al., 2014).

4.3 Major and Trace Element τ Values

Volumetric changes accompany weathering of basalt, which can complicate interpretations of concentration data. To overcome these complications, the mass balanced-based $\tau_{j,w}$ values have been adopted (Brimhall and Dietrich, 1987; Chadwick et al., 1990; Anderson et al., 2002). $\tau_{j,w}$ represents the percent mass change of a mobile element j, in a weathered sample relative to the mass of the same element in the parent rock (Anderson et al., 2002). It is calculated as

$$\tau_{j,w} = \frac{C_{j,w}C_{i,p}}{C_{j,p}C_{i,w}} - 1$$

where C represents the concentration of a mobile element, j, or an immobile element, i, in a weathered sample, w, or the parent rock, p. Nb is used as the immobile element in this study due to its documented immobility in basalt-derived soils (Hill et al., 2000; Kurtz et al., 2000; Liu et al., 2013). Negative $\tau_{j,w}$ values indicate a net loss of element, j, has occurred, while positive values indicate a net gain.

 $\tau_{j,w}$ values were calculated using major (Table 3.2) and trace (Table 3.3) element data for San Cristobal samples. As discussed previously, the Puerto Chino rock sample was collected and analyzed as a Cerro Colorado "parent" sample since we were unable to collect a fresh sample from Puerto Chino. However, the Puerto Chino sample displays anomalously low Nb values compared to both the other rock samples and the minimally weathered Puerto Chino samples. Thus, the rest of the rock samples were averaged, and that composition is used as a "parent" composition for calculating τ_j values for weathered Cerro Colorado samples. Additionally, while fresh parent samples were collected at the Socavòn, San Joaquin 2, and San Joaquin 1 sites, mineralogy and composition can vary throughout the thickness of a flow.

4.3.1 Alkaline Earths and Alkali Metals

Figure 3.5 shows τ_i values of Alkaline Earth elements and Alkali Metals in San Cristobal profiles. For Cerro Colorado samples, Mg is depleted up to 39%, while Ca is depleted up to 38% and Sr up to 26% (Figure 3.5a). In contrast, Ba is enriched up to 33%. For the Alkali Metals, Na behaves more like the Alkaline Earths exhibiting up to a 27% depletion, while K, Li, and Rb are enriched by up to 43%, 45%, and 67%, respectively. Mg, Ca, and Sr in Socavon samples exhibit maximum depletions from 97 to 99%, while Ba ranges widely from 66% depletion to 104% enrichment (Figure 3.5b). Na, K, and Rb are also depleted in Socavon samples up to 98%, 95%, and 83%, respectively, with only Li exhibiting enrichment (up to 204%). San Joaquin 2 samples show depletion of Na (up to 94%), Ca (up to 90%), Sr (up to 88%), K (up to 85%) and Mg (up to 84%; Figure 3.5c). Meanwhile, Rb ranges from 73% depleted to 10% enriched, and Ba ranges from 54% depleted to 33% enriched. Li is enriched up to 176%. For San Joaquin 1 samples, Na and Ca are depleted up to >99%, Rb and K up to 99%, Sr up to 97%, Mg up to 96%, and Li up to 76%. Ba ranges from 90% depleted to 46% enriched (Figure 3.5d). The El Junco grab sample exhibits, 97% depletion in Na, 95% in Ca, 93% in Mg, 92% in Sr, 87% in K, 82% in Rb, 76% in Ba, and 33% in Li.

Sample Name	Depth (cm)	Sample Type	Li	V	Cr	Co	Ni
Cerro Colorad	lo, Dry Zone						
CC-0	0	Soil	7.60	146.91	391.14	41.44	235.76
CC-10	10	Soil	8.60	132.46	324.58	35.93	191.44
CC-20	20	Rock	8.87	161.71	430.38	40.49	195.91
CC-40	40	Rock	8.19	151.55	418.68	43.42	271.21
CC-60	60	Rock	7.60	151.22	374.47	42.39	257.02
CC-80	80	Rock	8.79	158.59	391.63	40.30	223.90
CC-100	100	Rock	8.96	161.69	348.93	40.29	190.18
CC-120	120	Rock	8.56	158.19	384.23	40.30	220.86
CC-140	140	Rock	7.49	173.69	403.69	41.52	220.54
CC-160	160	Rock	8.09	166.67	475.08	45.57	269.99
Puerto Chino,	Dry Zone						
PC-R1	0	Fresh Rock	3.87	255.61	242.08	52.83	132.04
10111			0.07	200101	2.2.00	02100	102101
San Ioaquin 2	Transition to	Humid Zone					
SID 0		S all	6 70	202.26	002.01	02.26	501 12
SJ2-0	0	Soil	6.70	202.26	992.01	83.30	521.13
SJ2-10	10	Soll	7.58	190.80	//6.20	/4.96	408.07
SJ2-20	20	Soil	7.00	140.69	919.19	80.66	439.48
SJ2-30	30	Soil	6.29	125.21	8/1.26	69.35	393.07
SJ2-40	40	Soil	6.37	152.59	734.73	71.65	429.18
SJ2-50	50	Soil	8.17	140.20	853.08	73.59	454.84
SJ2-60	60	Saprolite	6.09	210.97	792.15	76.13	479.15
SJ2-70	70	Saprolite	6.50	221.04	748.56	69.40	436.95
SJ2-80	80	Saprolite	7.01	221.95	773.60	71.05	430.09
SJ2-90	90	Saprolite	8.59	236.17	728.47	93.65	548.98
SJ2-100	100	Saprolite	6.18	171.43	598.21	63.34	389.11
SJ2-110	110	Saprolite	7.52	250.29	867.91	78.41	514.46
SJ2-120	120	Saprolite	8.03	227.94	815.62	93.81	534.80
SJ2-130	130	Saprolite	7.17	220.74	857.11	86.59	570.69
SJ1-140	140	Saprolite	6.35	175.20	710.60	72.26	383.54
SJ2-150	150	Saprolite	7.43	161.15	679.45	69.20	362.43
SJ2-160	160	Saprolite	7.98	206.39	790.01	82.34	478.69
SJ2-170	170	Saprolite	6.67	198.13	699.69	89.93	465.22
SJ2-R2	0	Fresh Rock	2.64	244.13	685.74	58.18	343.24

Table 2.3. Trace Element Concentrations in Parts Per Million

Sample Name	Depth (cm)	Sample Type	Li	V	Cr	Co	Ni		
San Joaquin 1, Humid Zone									
SJ1-0	0	Soil	5.68	383.30	910.80	20.85	290.00		
SJ1-10	10	Soil	5.82	372.75	868.01	19.99	276.14		
SJ1-20	20	Soil	6.11	401.69	900.25	21.25	354.51		
SJ1-30	30	Soil	5.69	346.82	768.95	20.97	309.02		
SJ1-40	40	Soil	6.53	346.88	662.47	25.79	339.60		
SJ1-50	50	Soil	6.29	308.17	683.54	29.01	366.48		
SJ1-60	60	Soil	6.31	292.85	517.86	35.52	364.89		
SJ1-70	70	Soil	4.99	233.18	459.72	36.67	274.28		
SJ1-80	80	Soil	6.48	323.37	591.91	43.95	296.27		
SJ1-90	90	Soil	5.76	366.09	597.38	41.35	282.23		
SJ1-100	100	Saprolite	5.99	267.34	451.05	54.93	273.85		
SJ1-110	110	Saprolite	4.89	176.51	344.55	36.18	233.09		
SJ1-120	120	Saprolite	4.71	294.83	485.19	41.87	250.66		
SJ1-R1	0	Fresh Rock	11.45	193.24	293.76	37.07	155.91		
Socavòn, Dry	to Transition	Zone							
SV-0	0	Soil	15.97	344.74	1422.46	89.18	350.58		
SV-10	10	Soil	19.80	339.15	1195.88	88.23	369.98		
SV-20	20	Soil	19.53	324.06	1087.54	81.32	378.33		
SV-30	30	Soil	21.43	312.60	793.30	74.67	408.73		
SV-40	40	Soil	17.50	251.29	766.92	74.15	483.67		
SV-46	46	Saprolite	14.44	206.78	741.51	76.47	415.51		
SV-R1	0	Fresh Rock	4.48	237.86	667.52	55.40	289.07		
El Junco, Hur	nid Zone								
EJ-0	0	Soil	8.87	503.75	1897.35	62.31	539.43		
EJ-R1	0	Fresh Rock	4.36	249.84	665.64	57.29	304.29		

Table 2.3. Trace Element Concentrations in Parts Per Million, Continued



Figure 3.5. Variations in Alkaline Earth Element and Alkali Metal τ_j values with depth for samples from a. Cerro Colorado, b. San Joaquin 2, c. Socavòn, and d. San Joaquin 1. See text for details

4.3.2 Transition Metals and Phosphorous

 τ_i plots for transition metals and phosphorous in San Cristobal profiles are shown in Figure 3.6. Cerro Colorado samples are depleted in Cr up to 48%, V up to 47%, Ni up to 42%, Co up to 37%, Mn up to 28%, and Cu up to 16% depleted (Figure 3.6a). P ranges from 19% depleted to 12% enriched, and Pb is enriched up to 74%. In Socavon samples, P is depleted up to 76%, Mn up to 46%, V up to 41%, Cu up to 33%, and Co up to 17% (Figure 3.6b). Ni ranges from 34% depleted to 12% enriched, Cr from 24% depleted to enriched 19%, and Pb from 5% depleted to 106% enriched. San Joaquin 2 is depleted in P up to 94% and V up to 57% (Figure 3.6c). Cu ranges from 39% depleted to 24% enriched, Pb from 31% depleted to 45% enriched, Mn from 28% depleted to 22% enriched, Cr from 27% depleted to 22% enriched, Ni from 22% depleted to 36% enriched, and Co from 12% depleted to 36% enriched. San Joaquin 1 samples range from 78% depleted to 27% enriched in Mn, from 73% depleted to 45% enriched in Co, from 29% depleted to 98% enriched in Pb, from 13% depleted to 83% enriched in Ni, from 5% depleted to 50% enriched in V, and from 2% depleted to 98% enriched in Cu (Figure 3.6d). Samples are also enriched up to 63% in Cr and up to 255% in P. Ti, Al, Fe, and Y are traditionally considered to be more immobile than other transition metals and will be discussed in the next section. The El Junco grab sample is 67% depleted in Mn, 64% in Co, 42% in Ni, 34% in V, 33% in Cu and Li, but 113% enriched in P and 272% enriched in Pb.

4.3.3 Less Mobile/Immobile Elements

 τ_j plots are shown in Figure 3.7 for elements in San Cristobal profiles that are traditionally considered to be immobile or less mobile (HFSE + Y, Ti, Al, and Fe³⁺). Cerro Colorado samples are depleted up to 25% in Fe, up to 22% in Ti, and up to 10% in Al (Figure



Figure 3.6. Variations in Transition Metal and P τ_j values with depth for samples from a. Cerro Colorado, b. San Joaquin 2, c. Socavòn, and d. San Joaquin 1. See text for details.



Figure 3.7. Variations in immobile and less mobile element τ_j values with depth for samples from a. Cerro Colorado, b. San Joaquin 2, c. Socavòn, and d. San Joaquin 1. See text for details.

3.7a). In contrast, Ta is enriched up to 16%, Zr up to 46%, and Y up to 49%. For Socavòn samples, Y is depleted up to 55%, while Al ranges from 28% depleted to 11% enriched, Fe from 14% depleted to 9% enriched, Zr from 1% depleted to 11% enriched, and Ta is enriched up to 8% (Figure 3.7b). San Joaquin 2 samples range from 29% depleted to 35% enriched in Y, from 12% depleted to 20% enriched in Fe, from 11% depleted to 11% enriched in Ta, 9% depleted to 4% enriched in Ti, and from 8% depleted to 4% enriched in Zr, and from 4% depleted to 12% enriched in Al (Figure 3.7c). In San Joaquin 1 samples, Y is depleted up to 91%, while Al ranges from 20% depleted to 151% enriched, Zr from 12% depleted to 12% enriched, and Ta from 4% depleted to 20% enriched (Figure 3.7d). Finally, Fe is enriched up to 62% and Ti is enriched up to 65%. The El Junco grab sample exhibits 74% depletion in Y, 24% depletion in Al, 10 % depletion in Zr, 3% depletion in Fe, 1% depletion in Ta, and 2% enrichment in Ti.

4.4 Sr and Nd Isotopes

Isotope data for San Cristobal samples are given in Table 3.4. Most Cerro Colorado samples plot to close to the upper range of Sr isotopic values observed in the San Cristobal lava samples from this study and from White et al. (1993; Figure 3.8a). Sr isotopic values for Cerro Colorado samples from 0 cm to 40 cm are fairly consistent, except for a kick toward slightly higher values at 10 cm. From 40 cm to 120 cm, ⁸⁷Sr/⁸⁶Sr ratios decrease to values within the range of the unaltered rock samples at 120 cm. Isotopic ratios increase again at 160 cm, which is located near the contact between two flows and has the most radiogenic values in the profile. San Joaquin 2 soil samples from the top 30 cm of the profile plot to slightly more radiogenic Sr isotopic values than San Cristobal lava samples, but decrease to lava values by 50 cm and remain within the lava range throughout the bottom of the profile at 170 cm (Figure 3.8a). The Socavòn

Sample Name	Depth (cm)	Sample Type	⁸⁷ Sr/ ⁸⁶ Sr	$^{143}Nd/^{144}Nd$
Cerro Colorad	o, Dry Zone			
CC-0	0	Soil	0.703478	0.513058
CC-10	10	Soil	0.703615	0.513070
CC-20	20	Rock	0.703471	0.513046
CC-40	40	Rock	0.703498	0.513050
CC-80	80	Rock	0.703366	0.513044
CC-120	120	Rock	0.703174	0.513054
CC-160	160	Rock	0.703636	0.512818
Puerto Chino,	Dry Zone			
PC-R1	0	Fresh Rock	0.702785	0.513058
Socavòn, Dry	to Transition	Zone		
SV-0	0	Soil	0.705912	0.512977
SV-10	10	Soil	0.706100	0.512962
SV-20	20	Soil	0.706484	0.512965
SV-30	30	Soil	0.706184	0.512966
SV-40	40	Soil	0.705665	0.513009
SV-46	46	Saprolite	0.702917	0.513023
SV-R1	0	Fresh Rock	0.703293	0.513049
San Joaquin 2	, Transition to	Humid Zone		
SJ2-0	0	Soil	0.703435	0.513048
SJ2-10	10	Soil	0.703352	0.513045
SJ2-30	30	Soil	0.703454	0.513051
SJ2-50	50	Soil	0.703213	0.513060
SJ2-70	70	Saprolite	0.702929	0.513062
SJ2-90	90	Saprolite	0.703152	0.513058
SJ2-110	110	Saprolite	0.703041	0.513041
SJ2-130	130	Saprolite	0.702957	0.513059
SJ1-140	140	Saprolite	0.703228	0.513055
SJ2-150	150	Saprolite	0.703026	0.513059
SJ2-170	170	Saprolite	0.703097	0.513042

Table 3.4. Sr and Nd isotope ratios



Figure 3.8. a. 87 Sr/ 86 Sr and b. 143 Nd/ 144 Nd versus depth for San Cristobal samples. Two standard deviation error bars for Sr (±0.000012) and Nd (±0.00001) isotopes are smaller than the symbols. See text for details.

saprolite sample collected from the bottom of the profile (46 cm) also falls within the Sr isotope range exhibited by San Cristobal lavas, however, the top 40 cm of the profile have significantly more radiogenic ratios than any of the San Joaquin or Cerro Colorado samples.

Cerro Colorado samples from the upper 120 cm plot within the Nd isotope range of the San Cristobal lavas, however, the sample from 160 cm has the least radiogenic value $(^{143}Nd/^{144}Nd = 0.512828)$ of any sample in this study (Figure 3.8b). San Joaquin 2 soil and saprolite samples all fall within the San Cristobal lava range, as do the two Socavòn soil sample at 40 cm and the saprolite sample at 46 cm. However, the Socavòn soil samples from 0 cm to 30 cm exhibit significantly less radiogenic values than the lower Socavòn samples, the San Joaquin 2 samples, or the Cerro Colorado samples from the top 120 cm (Figure 3.8b).

5. Discussion

5.1 Intensity of Weathering at San Cristobal Sites

Cerro Colorado samples exhibit relatively low CIA values, minimal presence of alteration minerals, and are less depleted in the most mobile elements than the samples from the other sites, suggesting only incipient weathering has occurred. This is expected given the site's location in the dry zone, where there is limited precipitation to hydrolyze primary minerals.

Socavòn samples show very high CIA values, extensive depletion of mobile elements, and all primary igneous minerals have been converted to kaolinite and Fe oxides and oxyhydroxides. These suggest high intensity weathering has occurred, which was unexpected for the dry to transition zone Socavòn samples. However, the Socavòn site is located in the vicinity of the area that has been mapped as forming during the ~1 Ma to ~0.7 Ma Matuyama (Geist et al., 1986). Geist et al., (1986) determined the age groups used in their geologic map of San

Cristobal based on their own mapping of flow morphology combined with the paleomagnetic data collected along the northwestern and northeastern coasts by Cox (1971). Geist et al., (1986) did not discuss the scale at which San Cristobal flow morphology mapping was conducted, however the map in Figure 1 of their paper is at ~1:35,000 scale. Without knowing the how well constrained the contacts are, it is difficult to determine if the Socavòn site is located in Group 2 (Matuyama) or Group 3 (generally Brunhes). However, an older age for Socavòn lavas relative to the other sites could explain the high intensity of weathering despite the Socavòn site's dry to transition zone location.

San Joaquin 2 samples differ from the other humid zone sites in that they still have primary igneous minerals present, and most samples exhibit moderate loss of the most mobile elements and moderate CIA values suggesting a moderate degree of weathering. Samples from the San Joaquin 1 and El Junco sites have high CIA values, extreme depletion of mobile elements, and are composed of kaolinite and halloysite, goethite, hematite, and gibbsite, reflecting a very high weathering intensity.

Both San Joaquin 1 and 2 are located on the leeward side of the island in what has been mapped as the humid zone, however, they exhibit significant differences in extent of weathering. The highly weathered San Joaquin 1 site is located in the highlands (>500m), and thus is likely subject to the extensive cold-season stratus clouds that bring precipitation as both rainfall and fog. This would result in high humidity to the site. In contrast, the San Joaquin 2 site is at a lower elevation than the highlands, suggesting it would be less impacted by the fog, which is an important source of precipitation in the highlands (Percy et al., 2016). Thus, the San Joaquin 2 site would be drier, and therefore less weathered, than the San Joaquin 1 site.

5.2 Influence of Weathering and Mineralogy on Elemental Behaviors

5.2.1 Alkaline Earths and Alkali Metals

Ca, Sr, Na, and Mg, are the most leached elements in the profiles, reflecting increasing depletion with increasing weathering intensity due to progressive dissolution of the primary igneous minerals they are contained in Figure 3.6. Li is enriched in samples form Cerro Colorado, Socavòn and San Joaquin 2, likely due to incorporation of Li into secondary minerals (e.g., Penniston-Dorland et al., 2017 and references therein). However, it is depleted in San Joaquin 1 and El Junco, which is likely a result of the high precipitation at these sites and the solubility of Li. The trends of enrichment and depletion of Ba, Rb, and K can also be explained by the formation and destruction of secondary minerals that either incorporate those elements into their structure or adsorb them onto the surface.

A more detailed examination of mineralogical controls on elemental behavior in San Cristobal profiles may provide insight into the role of minerals, formed by differing extents of weathering under different climatic conditions, on elemental behavior in soils. In the incipient weathered Cerro Colorado profile, anorthite correlates negatively with τ_{Na} , τ_{Sr} , τ_{Ca} , and τ_{Ba} values ($R^2 = 0.51$, 0.86, 0.51, and 0.67, respectively; Figure A3.1a) suggesting Na leaching is greatest from areas with more abundant plagioclase. The correlation between τ_{Mg} values and mineral content ($R^2 = 0.78$; Figure A3.1b) suggests weathering of forsterite appears to be the primary factor controlling the behavior of Mg in the Cerro Colorado profile. The positive correlation for Mg may be due to the tendency of olivine to weather congruently (Chorover and Chadwick, 2001), and so loss of Mg would correspond to dissolution of olivine. In contrast, plagioclase can weather incongruently (Chorover and Chadwick, 2001), which may result in more plagioclase retention and a negative correlation. While other mobile elements showed

correlations with minerals identified by XRD, Li, K, and Rb did not. All three elements are incompatible in basaltic systems, and thus may be concentrated more in readily weathered glass than in minerals. Since the three elements are enriched in the samples (Figure 3.5a), they, along with Ba, must be retained by adsorption onto/incorporation into amorphous phases and/or secondary minerals not identified in the XRD analysis.

In the moderately-weathered San Joaquin 2 profile, only τ_{Ba} and τ_{Mg} values relate to primary mineral content, with both elements showing positive correlations with forsterite (R^2 = 0.41 and 0.56, respectively; Figure 3.2). τ_{Na} , τ_{Sr} , τ_{Ca} , and τ_{K} values all show negative correlations with Fe oxide and oxyhydroxide contents ($R^2 = 0.56$, 0.44, 0.50, and 0.49, respectively; Figure A3.3a and b). This may suggest they adsorb onto amorphous ferrihydrite, then partially desorb as crystallinity increases to form Fe oxides and oxyhydroxides. A significant decrease in adsorption capacity with increasing crystallinity was previously noted by Li and Zhou (2020) during the transformation to crystalline kaolinite from microcrystalline kaolinite and halloysite. Kaolin minerals seem to partially control retention of Li ($R^2 = 0.40$; Figure A3.4), however, adsorption onto amorphous phases and the possible presence of smectite not detected by the XRD analysis likely contribute to Li enrichment in the profile. Finally, as in the Cerro Colorado, τ_{Rb} values do not correlate with mineral content, which may suggest a lack of mineral preference for adsorption, a preference for a mineral phase not identified by XRD and/or a preference for amorphous phases. Unlike in the Cerro Colorado profile, Rb is depleted (Figure 3.5c). This may result from higher humidity promoting desorption of Rb and removal from the system.

The highly weathered, high humidity San Joaquin 1 samples show a positive correlation between τ_{Na} , τ_{Mg} , τ_{Li} , and τ_{Ba} values and gibbsite content ($R^2 = 0.86$, 0.68, 0.84, and 0.84, respectively; Figure A3.5) suggesting adsorption onto gibbsite plays a significant role in

retention of these elements. In contrast τ_{K} and τ_{Rb} values exhibit a negative correlation with gibbsite content ($R^2 = 0.61$ and 0.65; Figure A3.6a). A weaker positive correlation between τ_{K} and τ_{Rb} values and kaolin minerals ($R^2 = 0.46$ for both elements; Figure A3.6b) suggests a preference for kaolinite and halloysite followed by partial desorption during hydrolysis to gibbsite. However, the negative correlation with gibbsite is stronger than the positive correlation with kaolin minerals, which may suggest these elements adsorb onto amorphous and/or poorly crystalline phases as well, then partially desorb as crystallinity increases to form gibbsite. Additionally, τ_{Ca} values positively correlate with Fe oxides and oxyhydroxides ($R^2 = 0.47$; Figure A3.7), suggesting the minimal retention of Ca in the profile may be due to adsorption onto hematite and goethite. Finally, τ_{Sr} values do not correlate with minerals identified by XRD. This may suggest a lack of mineral preference for adsorption, a preference for a mineral phase not identified by XRD and/or a preference for amorphous phases.

For the highly weathered, dry to transition zone Socavòn samples τ_{Na} , τ_{Mg} , τ_{Sr} , and τ_{Ba} values all show positive correlations with Fe oxide and oxyhydroxide contents ($R^2 = 0.77$, 0.83, 0.86, and 0.81, respectively; Figure A3.8a and b). Since the Socavòn site is older than the others, the change from a negative correlation for Na and Sr in San Joaquin 2 samples to a positive one for Socavòn samples may reflect the eventual re-adsorption of these minerals following an initial desorption during the transition to greater crystallinity. This later re-adsorption was noted for kaolinite by Li and Zhou (2020). Meanwhile τ_K and τ_{Rb} values exhibit a negative correlation with Fe oxide and oxyhydroxide content ($R^2 = 0.76$ and 0.92; Figure A3.9). This is similar to the behavior of these elements with respect to gibbsite in the San Joaquin 1 profile, and again may suggest a preference for an amorphous/less crystalline phase over a more crystalline phase.

Finally, τ_{Ca} and τ_{Li} values do not show correlations with mineral content. For Ca, that may be due to extreme leaching, however, the enrichment of Li suggests adsorption onto/incorporation into amorphous phases and/or secondary minerals not identified in the XRD analysis.

5.2.2 Transition Metals and P

Dissolution of forsterite seems to exert the most control over transition metals and phosphorous in Cerro Colorado samples. τ_V , τ_{Cr} , τ_{Co} , τ_{Mn} , τ_P , and τ_{Ni} values correlate positively with forsterite content ($R^2 = 0.61, 0.52, 0.81, 0.50, 0.76$, and 0.80, respectively; Figure A3.10a and b). The positive correlation between τ_P and olivine content (R²=0.76; Figure A3.10b) was surprising. Glass dissolution would be expected to exert dominant control due to P incompatibility in minerals found in basalt, including olivine. However, Shea et al. (2019) note that $\leq 25^{\circ}$ C of undercooling can result in P enrichment in olivine, and that magma mixing under volcanoes is sufficient to cause this undercooling. Since P is also incompatible in plagioclase and pyroxene, an undercooling-induced enrichment in olivine may be enough to cause the observe correlation. However, adsorption of P onto olivine is also possible. Finally, τ_{Cu} and τ_{Pb} values do not correlate with the minerals identified by XRD, but have been documented to enter the lattice of more amorphous forms of ferrihydrite (Vodyanitskii, 2010). Thus, the presence of amorphous ferrihydrite in Cerro Colorado samples but not more crystalline Fe oxides and oxyhydroxides, may explain why τ_{Cu} and τ_{Pb} values do not correlate with mineral content as well as the better retention of these elements (Figure 3.6a).

In the moderately weathered, seasonally humid San Joaquin 2 samples, the role of forsterite is greatly decreased with only τ_{Ni} and τ_{V} values showing a positive correlation ($R^2 =$
0.52 and 0.59, respectively; Figure A3.11a). Additionally, a positive correlation between τ_P values and augite content suggests clinopyroxene may exert some control over P retention ($R^2 = 0.46$; Figure A3.11b), however this may be due to adsorption since P is incompatible in clinopyroxene. The negative correlation between τ_{Mn} values and Fe oxides and oxyhydroxides ($R^2 = 0.41$; Figure A3.12) suggests adsorption onto amorphous/poorly crystalline precursors to these more crystalline minerals, followed by partial desorption with increasing crystallinity, have replaced forsterite as the dominant control on Mn distribution. Meanwhile, τ_{Cr} , τ_{Cu} , τ_{Co} , and τ_{Pb} values do not correlate with any of the minerals quantified using the XRD. This could suggest a preference for amorphous phases, a preference for a crystalline phase not identified by XRD, and/or no preference for adsorption between the crystalline phases.

Gibbsite appears to be the dominant mineralogical control for samples from the highly weathered, high humidity San Joaquin 1 site. τ_P , τ_{Cu} , τ_{Mn} , τ_{Co} , and τ_{Ni} values show positive correlations with gibbsite content ($R^2 = 0.90$, 0.72, 0.77, 0.89, and 0.68, respectively; Figure A3.13a and b) suggesting adsorption onto gibbsite plays a significant role in their retention in the profile. τ_P values also show a trend of increasing enrichment with increasing depth. Given the location of the San Joaquin 1 profile near a potential agricultural/cattle grazing area, the presence of phosphate fertilizer or animal feces may explain the elevated P content. This P can then be redistributed as colloidal P which can be bound to nanoparticles of clay and Fe-(hydr)oxides or to Al-Fe-organic matter complexes (Regelink et al., 2011). The positive correlation with gibbsite content may suggest nanoparticles of gibbsite play a role in this downward translocation. In contrast, τ_{Pb} values correlate negatively with gibbsite ($R^2 = 0.71$; Figure A3.14a), suggesting preferential adsorption onto amorphous/poorly crystalline precursors followed by partial desorption with increasing crystallinity. A weak, positive relationship between kaolin minerals

and τ_{Pb} values ($R^2 = 0.35$; Figure A3.14b) may suggest some adsorption onto kaolinite and halloysite also plays a role. τ_V values negatively correlate with kaolin mineral content ($R^2 = 0.64$; Figure A3.15a) and show a weaker positive correlation with gibbsite ($R^2 = 0.42$; Figure A3.15b). This may also suggest adsorption during/after hydrolysis of kaolinite to gibbsite. Finally, τ_{Cr} values do not correlate with any of the minerals quantified using XRD.

In samples from the highly weathered, dry to transition zone Socavon site, Fe oxides and oxyhydroxides and their amorphous precursors exert the dominant mineral control over transition element distribution. τ_V , τ_{Mn} , and τ_{Pb} values exhibit a negative correlation with goethite $(R^2 = 0.93, 0.46, and 0.88, respectively; Figure A3.16a)$, which may suggest a preference for an amorphous phase, followed by partial loss of the element as crystallinity increases. Ferrihydrite, an amorphous/poorly crystalline predecessor for the Fe oxides and oxyhydroxides, fixes many heavy metal cations including Mn and Pb (Vodyanitskii, 2010). This, along with adsorption, could account for the presence of these elements in amorphous phases. In contrast, τ_{Co} , and τ_{Cu} values exhibit a positive correlation with Fe oxides and oxyhydroxides ($R^2 = 0.65$ and 0.87, respectively; Figure A3.16b), suggesting a preference for the more crystalline phase. Adsorption onto the surface of the Fe oxides and oxyhydroxides likely plays a major role, especially for Co. However, Cu has been documented to enter the more amorphous forms of ferrihydrite and be retained during the transformation to minerals such as goethite (Vodyanitskii, 2010). The potential presence of Cu in the crystal structure of Fe oxides and oxyhydroxides, in addition to surface adsorption, may account for the stronger positive correlation of Cu relative to Co. τ_{Ni} values show a positive correlation with kaolin mineral content ($R^2 = 0.49$; Figure A3.17), which may suggest adsorption of Ni onto kaolinite and halloysite plays a role in the element's retention. Finally, P and Cr do not correlate with any of the mineral phases. This could mean they adsorb

onto all of the minerals without preference, prefer amorphous phases, and/or prefer minerals not quantified by XRD.

5.2.3 HFSE and Other Traditionally Immobile Elements

Incipiently weathered, dry zone Cerro Colorado samples do not show any correlations between τ_{Ti} , τ_{Al} , τ_{Fe} , τ_{Ta} , and τ_{Y} values and mineral content. As noted by (Babechuk et al., 2015) immobile elements are often hosted in accessory minerals that are resistant to weathering. This may suggest the presence of accessory mineral(s) that were missed during XRD data processing. Additionally, Hill et al. (2000) notes that, while Y has traditionally been considered to be immobile, it can be redistributed during early stages of weathering. Thus, Y may be less likely to be retained in a resistant accessory mineral, and the lack of trend may be related to adsorption onto amorphous phases. τ_{Zr} values were the only ones that correlated with identified mineralogy, showing a positive correlation with augite ($R^2 = 0.75$; Figure A3.18). Augite is less susceptible to chemical weathering than olivine which may account for the enrichment of Zr in the Cerro Colorado profile.

As with the Cerro Colorado profile, San Joaquin 2 samples do not show a correlation between crystalline minerals and τ_{Ti} , τ_{Fe} , τ_{Ta} , and τ_{Y} values, likely due to their presence in unidentified accessory minerals (Ti, Fe, Ta) and adsorption onto amorphous phases (Y). However, τ_{AI} values correlate negatively with Anorthite + Augite content ($R^2 = 0.61$; Figure A3.19a), suggesting greater abundance of those minerals leads to increased Al leaching. The slight enrichment of Al in some areas of the profile (Figure 3.7c) suggest retention by incorporation into/adsorption onto a combination of secondary minerals and amorphous phases. Finally, τ_{Zr} values show a negative correlation with anorthite ($R^2 = 0.46$; Figure A3.19b). For

other elements, a negative correlation with anorthite content has been interpreted as increased loss due to leaching in areas of greater anorthite abundance. However, an explanation involving leaching of anorthite is suspect because Zr is highly incompatible in that mineral, and thus would not be present in notable quantities. Additionally, chemical weathering of anorthite seems to be in contrast to the relatively consistent τ_{Zr} values. A better explanation maybe that, in this instance, correlation is not causation.

In samples from the high humidity San Joaquin 1 profile, gibbsite appears to exert a significant control on elemental distribution, exhibiting positive correlations with τ_{AL} , τ_{T1} , and τ_{Y} values ($R^2 = 0.90$, 0.52, and 0.60, respectively; Figure A3.20a). Meanwhile, τ_{Fe} , τ_{Zr} , and τ_{Ta} values do not correlate with identified minerals, which may suggest they are hosted in resistant accessory minerals not identified during XRD data processing. Additionally, τ_{A1} values show Aldepletion for the top portion of the profile, and Al-enrichment toward the bottom of the profile. The area of maximum Al₂O₃-accumulation (up to 151%; Figure 3.7d) and maximum gibbsite content (up to 60%; Table 3.1b) both occur in the upper saprolite near the soil-saprolite interface, suggesting downward translocation of Al. Given the strong correlation between gibbsite content and Al retention ($R^2 = 0.90$; Figure A3.20a), nanoparticles of gibbsite may be transporting the Al down-profile.

However, this may not be the only mechanism producing the significant Al enrichment and high gibbsite content just below the soil/saprolite boundary. The upper saprolite area can be a zone of maximum kaolinite hydrolysis (Jiang et al., 2018). Thus, Si-Al clay minerals such as kaolinite may transport Al downward (Regelink et al., 2011), at which point gibbsite may form by hydrolysis of the clay minerals (Jiang et al., 2018). This process likely contributes to the downward translocation Al, as evidenced by the negative correlation between τ_{Al} values and kaolin mineral content ($R^2 = 0.45$; Figure A3.20b), and may also contribute to the high gibbsite concentration in the upper saprolite. Additionally, decomposition of organic material in the upper portion of the profile may produce organo-mineral colloids (Pokrovsky et al., 2006) which improve mobilization and downward transportation of elements like Al through Al-organic matter complexes (Ma et al., 2007; Regelink et al., 2011). The result is a depletion in the immobile element in the top of the profile and an enrichment in the bottom, as is observed for Al at the San Joaquin 1 site. The Al in solution may also precipitate to form gibbsite (Hill et al., 2000), thus further contributing to the gibbsite enrichment lower in the profile.

Kaolin minerals and Fe oxides and oxyhydroxides both appear to play a significant role in retention of traditionally immobile elements in the older, dry zone samples of the Socavòn profile. τ_{Ti} , and τ_{Fe} values correlate positively with Fe oxides and oxyhydroxides (R² = 0.52 and 0.57, respectively; Figure A3.21a), suggesting incorporation into these minerals controls Ti and Fe retention. Meanwhile, τ_{Ta} values show a negative correlation with hematite (R² = 0.65; Figure A3.21b). This may indicate the accessory mineral controlling Ta retention ultimately weathers to hematite. τ_{Zr} values correlate positively with kaolin mineral content (R² = 0.60; Figure A3.21b), suggesting retention by adsorption onto kaolin mineral surfaces. While Zr is considered an immobile element, local redistribution of Zr may occur during high degrees of weathering (Hill et al., 2000). In contrast, τ_Y values correlate negatively with kaolin mineral content (R² = 0.65; Figure A3.22), suggesting a preference for the less crystalline precursors to kaolinite and halloysite, followed by partial adsorption as crystallinity increases. Finally, τ_{Al} values do not correlate with mineral content, but do show a trend of Al-enrichment lower in the profile suggesting downward translocation of Al. This downward translocation may occur by Al-organic colloids such as those described for the San Joaquin 1 profile, however, the Al may precipitate out of solution as amorphous phases given the lack of correlation with kaolin minerals.

5.2.4. Comparison to Basalt Weathering in Other Areas

The relative lack of quantitative mineralogy for soil profiles weathered on basalt provides a challenge for comparing this study's results to other papers, especially for the Cerro Colorado and San Joaquin 2 profiles which contain primary igneous minerals. Chadwick et al. (2003) published quantitative data on the < 2 mm size fraction for 0.41 to ~ 0.14 Ma arid, transisition, and humid zone samples from the island of Hawaii. The data were collected using sequential extractions and group gibbsite, hematite, and goethite under "crystalline sesquioxides", futher complicating comparisons. Additionally, the sequition extraction data include phases such as organic material. Thus, the crystalline phases from the sequence extraction data were renormalized to 100% to make them comparable to the XRD data, which do not include noncrystalline phases such as organics in the quantitative analysis. Semi-quantitative XRD data are available only for the <0.002 mm size fraction of Chadwick et al. (2003). These results likely do not reflect the detailed mineralogy of the extraction data, but provide some insight into the sesquioxides that may be present. The XRD data suggest trace amounts of gibbsite are present in most horizones at arid site B and humid site M. Trace amounts of hematite are present in most horizons at arid site B, but only sporatically present in arid site E, transistion sites I and J, and absent from the <0.002 mm fraction at humid site M. Goethite was not detected in that size fraction for any of the sites, though it may be present in the silt and sand-sized fractions. XRD data were not given for humid site L. Nelson et al. (2013) published quantitaive XRD data for a transition zone profile on the island of Oahu, Hawai, with a parent lava composition averaged

from Haskins and Garcia (2004). Quantitative XRD for profiles weathered under humid conditions were avaliable for three 0.303 Ma Hawaiian laterite profiles (Sowards et al., 2018), and two 17 Ma to 6 Ma Columbia River basalt profiles (Liu et al., 2013). Due to the variability in available elemental data, τ_j values for Sowards et al. (2018) and Nelson et al. (2013) are calculated with Ti as the immobile element, while Chadwick et al. (2003) use Zr and τ_j values for Liu et al. (2013) were calculated relative to Nb. All mineral percentages represent the percent of a mineral relative to crystalline phases and do not include amoprhous or poorly crystalline phases.

The arid zone profiles from Chadwick et al. (2003) are significantly more weathered than the Cerro Colorado samples making comparissons difficult. This is evidenced by the presence of kaolin minerals and sesquioxides in the Chadwick et al. (2003) samples and the lack of primary minerals. In contrast, crystalline phases in the Cerro Colorado profile are composed almost entirely of primary igneous minerals. The Cerro Colorado profile had a very thin layer of soil whose τ_i values do not differ significantly from the underlying cohesive rock. It is possible given the Cerro Colorado profile's location in an abandoned quarry that a thicker, more weathered soil profile once existed but was lost during quarrying, however, the lack of a saprolite layer between the soil and the cohesive rock argues against this. Correlations for Chadwick et al. (2003) profile E samples suggest kaolin minerals influence retention of K, Na, Ca, and Mg ($R^2 = 0.46, 0.52$, 0.51, and 0.53, respectively; Figure A3.23a), while no preference was shown for Al. Meanwhile profile B samples do not exhibit correlations with crystalline phases. However, the original sequence extraction data for the 2Cr1 horizon show suspiciously low percentages for all components. If the data from that horizon are excluded, the remaining data suggest sesquioxides may control Al retention ($R^2 = 0.86$) while the amorphous/poorly crystalline precursors to the

sesquioxides seem to influence Ca, Na and K retention ($R^2 = 0.91$, 0.66, and 0.62; Figure A3.23b).

Seasonally humid San Joaquin 2 samples were compared to one transition zone profile from Nelson et al. (2013) and two from Chadwick et al. (2003). These profiles were selected to best approximate the seasonal humidity and moderate weathering of the San Joaquin 2 site. Despite this, all of the comparison profiles are more weathered than the San Joaquin 2 samples, as evidenced by the lack of primary igneous minerals in all three profiles. The inverse correlation San Joaquin 2 samples show between τ_{Na} values and hematite + goethite content (R² = 0.56) is also found in data from Nelson et al. (2013) ($R^2 = 0.56$; Figure A3.24a), suggesting retention by amorphous to poorly crystalline phases in these profiles. Both sites I and J from Chadwick et al. (2003) shows a positive correlation between τ_{Na} values and sesquioxide minerals ($R^2 = 0.54$ and 0.43, respectively; Figure A3.24b). Presuming the sesquioxides are largely Fe oxides and oxyhydroxides, the change from positive correlations for the younger Chadwick et al. (2003) samples to negative correlations in the older profiles from Nelson et al. (2013) and this study may be due to desorption over time, perhaps as crystallinity increases. The negative correlations between τ_{Ca} and τ_{K} and hematite + goethite ($R^2 = 0.50$ and 0.49, respectively) seen in San Joaquin 2 samples (Figure A3.3) are not observed in any of the transition or humid zone profiles. However, a positive correlation between $\tau_{\rm K}$ and hematite + goethite in the ~3.2 Ma to 1.8 Ma transition zone profile from Nelson et al. (2013) ($R^2 = 0.52$) may suggest eventual re-adsorption (Figure A3.25). Mineralogical preferences for Mg range from forsterite in San Joaquin 2 ($R^2 =$ 0.56; Figure A3.2) to sesquioxides in Chadwick et al. (2003) profile J ($R^2 = 0.55$; Figure A3.26a) and kaolin minerals in Nelson et al. (2013) ($R^2 = 0.74$; Figure A3.26b). Chadwick et al. (2003) profile I did not exhibit correlations between Mg retention and mineralogy.

Unlike in San Joaquin 2 samples where Mn may be controlled by amorphous/poorly crystalline precursors to hematite + goethite (Figure A3.12), correlations suggest a preference for crystalline kaolin minerals in the Nelson et al. (2013) profile ($R^2 = 0.78$; Figure A3.27), and no preference at the Chadwick et al. (2003) transition zone sites. Kaolin minerals also may control P retention in the Nelson et al. (2013) profile ($R^2 = 0.60$; Figure A3.27), while no preference for P is observed in samples from Chadwick et al. (2003) or this study. For more immobile elements, San Joaquin 2 correlations suggest anorthite and augite weathering control Al retention (Figure A3.19). However, these minerals are not present in the transition zone profiles of Chadwick et al. (2003) and Nelson et al. (2013). Instead, profile I from Chadwick et al. (2003) suggests a preference for sesquioxides ($R^2 = 0.68$; Figure A3.28a) while the Nelson et al. (2013) and profile J from Chadwick et al. (2003) suggests retention by kaolin minerals ($R^2 = 0.66$ and 0.89, respectively; Figure A3.28b). Finally, neither the San Joaquin 2 samples or the profiles from Chadwick et al. (2003) and Nelson et al. (2013) indicate a preference for Fe retention.

San Joaquin 1 samples were compared to humid zone profiles from Chadwick et al. (2003), Liu et al. (2013), and Sowards et al. (2018). Only profiles M and J from Chadwick et al. (2003) show correlations between τ_{Ca} and mineralogy. Profile M corelates positively with kaolin minerals ($R^2 = 0.62$; Figure A3.29), while profile L correlates negatively with sesquioxides ($R^2 = 0.55$; Figure A3.29). Profiles from Sowards et al. (2018), Liu et al. (2013), and the San Joaquin 1 site do not show correlations between mineralogy and Ca retention. Data from the San Joaquin 1 samples suggest gibbsite controls Na retention ($R^2 = 0.86$; Figure A3.5). Meanwhile, data from profile L of Chadwick et al. (2003) correlate negatively with sesquioxides, which may include gibbsite ($R^2 = 0.59$; Figure A3.30a). Data from profile 3 from Sowards et al. (2018) show a negative correlation between τ_{Na} and kaolin minerals + gibbsite ($R^2 = 0.68$; Figure A3.30b),

while data from the Cowlitz profile of Liu et al. (2013) shows a positive one ($R^2 = 0.60$; Figure A3.30b). The change from negative to positive correlation with age may result from an initial desorption of Na with increasing crystallinity, followed by an eventual re-adsorption. For profiles that show correlations between gibbsite ± kaolin minerals and Na, those correlations change from a negative in the younger profiles of Chadwick et al. (2003) and Sowards et al. (2018) to positive in the older profiles of Liu et al. (2013) and this study.

In older profiles, Mg retention seems to be largely controlled by gibbsite \pm kaolin minerals as observed in the San Joaquin 1 profile (R² = 0.68; Figure A3.5), and the Cowlitz (R² = 0.54; Figure A3.31a) and Columbia (R² = 0.70; Figure A3.31a) profiles of Liu et al. (2013). In contrast, hematite + goethite may be the primary influence on Mg retention in the younger Profile 1 of Sowards et al. (2018) (R² = 0.48; Figure A3.31b). In profiles that show mineralogical correlations with K, those correlations tend to be negative, suggesting a preference for amorphous/poorly crystalline precursors to gibbsite and kaolin minerals. This can be observed in correlations between τ_{K} and gibbsite in the San Joaquin 1 profile (R² = 0.61; Figure A3.6a); τ_{K} and gibbsite \pm kaolin minerals in the Cowlitz (R² = 0.81; Figure A3.32); τ_{K} and kaolin minerals in Chadwick et al. (2003) profile M (R² = 0.63; Figure A3.32); and between τ_{K} and hematite + goethite in Sowards et al. (2018) profile 1 (R² = 0.56; Figure A3.32).

P shows positive correlations with gibbsite \pm kaolin minerals in the older San Joaquin 1 profile (R² = 0.90; Figure A3.13) and the Columbia and Cowlitz profiles of Liu et al. (2013) (R² = 0.44 and 0.67, respectively; Figure A3.33) but does not show correlations in the younger profiles of Sowards et al. (2018). Meanwhile, Mn retention positively correlates with gibbsite in this study (R² = 0.77; Figure A3.13) and kaolin minerals in profile 2 of Sowards et al. (2018) (R² = 0.55; Figure A3.34). For those profiles that show mineralogical correlations for the more immobile elements, Al and Ti tend to correlate positively with gibbsite ± kaolin minerals. τ_{Al} values correlate positively with gibbsite in the San Joaquin 1 profile (R² = 0.90 Figure A3.20a) and the Sowards et al. (2018) profile 1 (R² = 0.42; Figure A3.35a), with sesquioxides which may include gibbsite in Chadwick et al. (2003) profile L (R² = 0.80; Figure A3.35a) and with kaolin minerals + gibbsite in the Cowlitz and Columbia cores of Liu et al. (2013) (R² = 0.81 for both; Figure A3.35b). Meanwhile Ti retention correlates positively in gibbsite for data from San Joaquin 1 (R² = 0.52; Figure A3.20a) and the Liu et al. (2013) Columbia core (R² = 0.55; Figure A3.36), while τ_{Ti} values in the and the Liu et al. (2013) Cowlitz core correlate positively with gibbsite + kaolin minerals (R² = 0.64; Figure A3.36). Fe does not show mineralogical correlations for any of the sites examined. P, Mn, Fe, and Ti data were not given for the Chadwick et al. (2003) profiles.

The older, transition zone samples of the Socavòn profile were compared to the ~3.2 Ma to 1.8 Ma transition zone profile Nelson et al. (2013). As with the Socavòn data, τ_{Ca} values for the Nelson et al. (2013) profile do not correlate with mineralogy. The positive correlation Socavòn samples show between τ_{Na} values and hematite + goethite content ($R^2 = 0.77$; Figure A3.8a) is negative for Nelson et al. (2013) ($R^2 = 0.47$; Figure 2.37a), which may suggest eventual desorption given the age of the Nelson et al. (2013) samples. Correlations between τ_K values and hematite + goethite content are also inverse for this study and Nelson et al. (2013), with the Socavòn samples showing a negative correlation ($R^2 = 0.76$; Figure 2.9) and the Oahu samples showing a positive one ($R^2 = 0.52$; Figure 2.37a). τ_{Mg} , τ_{Mn} , τ_P , and τ_{A1} values in the Nelson et al. (2013) samples positively correlate with kaolin minerals ($R^2 = 0.74$, 0.78, 0.60, and 0.66, respectively; Figure A3.37b). This differs from the Socavòn profile in which Mg and Mn seem to prefer hematite + goethite and their amorphous precursors ($R^2 = 0.82$ and 0.46,

respectively; Figure A3.8a and A2.16a, respectively). However, the transition zone profile from Nelson et al. (2013) receives ~1,500 mm/yr of rainfall, whereas the altitude of the Socavòn site is expected to receive < ~1,000 mm/yr Lasso and Espinosa (2018). This difference in humidity could influence the enhanced role of kaolin minerals, particularly halloysite, in the Nelson et al. (2013) samples. Finally, the Oahu profile does not show a mineralogical preference for Fe, unlike the Socavòn profile where Fe correlates with hematite + goethite content ($R^2 = 0.52$; Figure A3.21).

5.2.5 Implications of Changing Climate for Mineralogical Controls on Elemental Retention

The Galapagos provide a natural laboratory for studying how variations in mineralogy due to differing climates and weathering intensities impact elemental retention in soils of similar age and substrate. Thus, the results of this study can provide insight into how weathering may progress as climate changes, especially when compared to data from other authors. Additionally, results from the older Socavòn profile suggest how weathering in drier areas may progress with time.

When the impact of climate is examined, results suggest that incongruent weathering of plagioclase and congruent weathering of olivine and glass dominate mobile element distribution in dry climates where only incipient weathering has occurred. This may be due to the high susceptibility of olivine and plagioclase to chemical weathering. Olivine also seems to exert the dominant control over P and most of the transition elements, with amorphous ferrihydrite contributing to a lesser extent. Immobile elements are likely controlled mostly by a resistant accessory phase that was not identified during XRD data processing; however, augite may contribute to Zr retention. It is interesting to note that Hawaiian arid zone samples from

Chadwick et al. (2003) are significantly more weathered than the Cerro Colorado profile despite being younger. It is possible a more weathered soil profile once excisted at the Cerro Colorado site but was lost during quarrying. If this is the case, the implications of the Cero Colorado data on dry zone weathering could be more limited.

As humidity and the resulting weathering intensity increase, the importance of readily weathered primary minerals in element retention decreases, with amorphous phases likely playing an important role for many mobile, transition and immobile elements. However, olivine weathering may still influence Ni and V, while P adsorption onto augite and Al leaching from anorthite and augite may influence those elements. Secondary minerals such as Fe oxides and oxyhydroxides and kaolin minerals play a more minor role, promoting retention of Mn, Li, and possibly playing a role in Al retention. However, these secondary minerals increase in importance as weathering progresses under transition zone conditions.

Finally, as high humidity and weathering intensity are reached, gibbsite, and to a lesser extent its amorphous/poorly crystalline precursors, become the dominant control on the distribution of most mobile and transition elements as well as P, Ti, Al, and Y in San Joaquin 1samples. Meanwhile the role of Fe oxides and oxyhydroxides appears to be significantly less important. Kaolin minerals also seem to be less significant in controlling element distribution in humid zone profiles from this study. However, data from other studies of basalt weathering under humid conditions (Liu et al., 2013; Sowards et al., 2018) suggest kaolin minerals work in concert with gibbsite to aid in element retention. Thus, the role of kaolinite and halloysite in humid climates should not be discounted.

Socavon samples suggest that, in older, highly weathered samples from drier climates, Fe oxides and oxyhydroxides, and/or their amorphous precursors, may control distribution of most

mobile and transition elements as well as P, Fe, Ti, and Ta. This is also suggested for Na and K by data from Nelson et al. (2013). Meanwhile, kaolin minerals may exert primary control on retention of Mg, Mn, P, and Al in the Nelson et al. (2013) samples, while only Y and Zr seem to be controlled by kaolin minerals in the Socavòn profile. The difference significance of kaolin minerals between the Socavòn site and the Nelson et al. (2013) Oahu profile may result from the increased humidity at the latter location.

5.3 Other Contributions to San Cristobal Samples

5.3.1 Isotopic Parent Composition for San Cristobal Mixing Models

This study uses the Socavòn rock sample to represent the parent rock composition for Sr and Nd mixing models. The San Joaquin 2 rock was collected as the parent rock composition for the San Joaquin 2 site, however, the aliquot sent for isotopic analysis lost during dissolution, and thus isotopic data are not available. REE data indicate the Puerto Chino rock sample, originally collected as a parent composition for the Cerro Colorado site, is more geochemically similar to rocks collected by White et al. (1993) from the northeastern side of the island than it is to rock samples from the southwestern side of the island where sampling for this study was focused (Figure A3.38). Cerro Colorado samples have experienced minimal alteration, as evidenced by their XRD mineralogy and relatively unaltered MIA and CIA values enabling REE patterns for the Cero Colorado samples to be compared to the Puerto Chino and Socavòn rocks (Figure A3.38). These data indicate the Cerro Colorado samples resemble rock REE patterns for the southwestern side of the island, as represented by the Socavòn rock, and are not consistent with REE compositions from the northeaster side of the island and the Puerto Chino sample. Thus, the Puerto Chino rock sample is ruled out and the Socavon rock is used as the endmember composition for modeling Cerro Colorado samples.

5.3.2 Marine Aerosol Influence

Sr isotope ratios of Socavòn samples from the top 40 cm of the profile plot to significantly heavier values than the Cerro Colorado and San Joaquin 2 samples (Figure 3.8a). Preferential leaching of ⁸⁷Sr during high intensity weathering and nutrient biolifiting of ⁸⁶Sr from depth can be eliminated as potential causes for the heavier Socavòn samples because both produce an isotopically lighter residue (Bullen and Chadwick, 2016). However, most water vapor in the atmosphere is formed by the evaporation of seawater, and as a result atmospheric deposition of marine aerosols, formed by evaporation of hydrated and/or dissolved ocean-derived salts, can be important sources of some cations in soil profiles (Derry and Chadwick, 2007). These marine aerosols can be approximated using seawater (Vitousek et al., 1999), which has a heavier Sr isotopic signature and lower Sr concentration than Socavòn rocks (Paytan et al., 1993). Thus, a marine aerosol influence likely causes the low [Sr], isotopically heavy, Socavòn samples.

5.3.3 Volcanic Ash and Eolian Dust Influence

Samples from the top 30 cm of the Socavon profile, and the 160 cm Cerro Colorado sample display significantly lower ¹⁴³Nd/¹⁴⁴Nd ratios compared to the other San Cristobal samples with isotopic data from this study and White et al. (1993). Fractionation of Sm from Nd occurs during weathering, however, Babechuk et al. (2014) indicate this would not impact modern profiles, and calculated a change of 1 ɛNd unit over 1 billion years based on

fractionation in samples from the Chhindwara profile. Given the age of Galapagos lavas, Sm/Nd fractionation cannot account for the Nd isotopic variations of the Galapagos soil and saprolite samples. Thus, mixing of another component with the Socavòn parent rock is required to explain the Nd isotopic compositions of the Socavòn samples from the top 30 cm and the Cerro Colorado sample from 160 cm.

The marine aerosols that dominated Sr isotopic signatures are not candidates for Nd isotope mixing endmembers due to the extremely low Nd concentration in seawater. However, the proximity of the Galapagos to the mainland of South America makes the Ecuadorian volcanoes potential contributors of ash to San Cristobal island. The volcanoes from the other Galapagos islands, including the currently active volcanoes of Isabela Island, are not likely contributors due to the southeasterly trade winds, which are the dominant winds in the Galapagos. The strength of the trade winds is impacted by the migration of the Intertropical Convergence Zone (ITCZ), with stronger winds when the ITCZ is in its more northerly position, and weaker winds when the ITCZ migrates south leaving the Galapagos islands almost in the doldrums (Trueman and D'Ozouville, 2010). Research indicates the ITCZ also migrated southward due to cooler water temperatures during the last Glacial Maximum, producing weaker trade winds during those periods (Koutavas and Lynch-Stieglitz, 2003). Gili et al. (2017) suggest the southern westerly winds (\sim 50°S) and the high-altitude subtropical westerly jet stream (~30°S), both migrated north during glacial periods (See Figure 7 of Gili et al., 2017). However, Gili et al.'s (2017) model does not indicate this migration would impact wind direction at the equator. Thus, the predominant southeasterly wind direction along with San Cristobal's location as the eastern-most island, can be used to exclude other Galapagos volcanoes as likely contributors of ash to San Cristobal while supporting mainland volcanoes as potential sources.

In addition to ash from the South American volcanoes, eolian dust is another potential endmember for the lower ¹⁴³Nd/¹⁴⁴Nd samples. The Northern Hemisphere has more landmass than the Southern Hemisphere, and therefore generates the majority of eolian material (Xie and Marcantonio, 2012), with Asian loess being particularly significant source of Pacific dust (Nakai et al., 1993). Other potential dust sources to the Equatorial Pacific could include Africa, Australia, and South America (Xie and Marcantonio, 2012). Nakai et al. (1993) concluded that eolian deposition in the eastern equatorial Pacific is characterized by material consistent with northwestern South America instead of the loess from Asia or North America that has been noted in other areas of the Pacific. The authors attributed the lack of non-South American dust to the location being downwind of the ITCZ, which could form a barrier to transport of eolian material. However, Xie and Marcantonio (2012) conclude that during glacial times northern hemisphere eolian material could be deposited south of the ITCZ. They suggest loess from Asia or the Sahara to explain more radiogenic Nd isotope signatures in the northern-most samples (1.3°N to 7.21°N), and Australia dust for the unradiogenic ¹⁴³Nd/¹⁴⁴Nd ratios their southern-most site (3°S). However, Xie and Marcantonio's (2012) transect is located at 110°W, which is significantly west of San Cristobal, and the sites with the proposed Northern hemisphere and Australian dust contribution are north and south, respectively, of the San Cristobal sites, which lie ~0.9°S of the Equator. While it may be possible that dust from Australia, the Sahara, or Asia is reaching San Cristobal Island during interglacial periods, Nd isotope ratios of these areas largely overlap with those of South American loess, the latter of which seems a more likely source given the closer proximity of the Galapagos islands to the South American mainland, and the dominant southeasterly wind direction. Thus, South American loess from Gili et al. (2017) is used for mixing models instead of loess from other sources.



Figure 3.9. Mixing Scenarios for a. Socavon samples and b. the Cerro Colorado 160 cm sample. Two standard deviation error bars for Nd isotopes (± 0.00001) are smaller than the symbols. See text for details

Table 3.5. Mixing Model Parameters.

	Nd (ppm)	143Nd/144Nd									
Ash - Basalt Mixing Scenario 1											
Antisana sample 1 ^a	52.8	0.512845									
Socavòn Rock	16.02	0.513049									
Ash - Basalt Mixing Scenario 2											
Antisana Sample 2 ^b	34	0.51275									
Socavòn Rock	16.02	0.513049									
Ash - Basalt Mixing Sc	enario 3										
Pre-Caldera Chacanab	27.5	0.512548									
Socavòn Rock	16.02	0.513049									
Dust - Basalt Mixing S	cenario										
South American Dust ^c	52.7	0.512113									
Socavòn Rock	16.02	0.513049									
^a Bryant et al. (2006)											
^d Hidalgo et al. (2012)											
°Gili et al. (2017)											

Nd concentration versus ¹⁴³Nd/¹⁴⁴Nd ratio mixing models are shown for Socavòn samples from the top 30 cm in Figure 3.9a, with endmember compositions given in Table 3.5. The mixing scenarios use two different ash compositions from the Antisana volcano in Ecuador (Bryant et al., 2006; Hidalgo et al., 2012), which suggest between 20% to 25% ash component mixed with the Socavòn basalt endmember. The 40 cm sample may also have a small (~4%) dust influence. The values for the top 30 cm are within the range of Liu et al. (2013) who noted 20% to 60% dust addition to laterites formed on the Columbia River basalt. A dust-derived component in the Socavòn profile is also supported by the presence of cristobalite, which XRD data indicate represents ~18% to ~23% of crystalline phases in samples from the top 30 cm. XRD analysis indicates cristobalite is not present in the rock samples or in the soil samples with Nd isotopic values similar to those of the rocks. Additionally, attributing up to ~23% quartz from eolian sources is in line with the findings of Kurtz et al. (2001), who attributed the up to 30% quartz in their Hawaiian samples to Asian dust and with. The majority of dust compositions from Gili et al. (2017) do not, as a pure endmember, explain the lower ¹⁴³Nd/¹⁴⁴Nd Socavòn samples, however they cannot be ruled out as a mixed contribution with dominantly volcanic ash.

The 160 cm Cerro Colorado sample also displays notably lower ¹⁴³Nd/¹⁴⁴Nd values than the rest of the San Cristobal samples. While the Cerro Colorado site is composed mostly of coherent rock, the 160 cm sample was collected from an area that looks like a contact between two lava flows. Mixing models suggests the sample's ¹⁴³Nd/¹⁴⁴Nd ratio can be explained by mixing of basalt with ~35% ash of similar composition to the pre-caldera eruption phase of Ecuador's Chacana volcano, or ~10% input from South American Eolian deposits (Figure 3.9b). Unlike the upper Socavon samples, the 160 cm Cerro Colorado sample does not have significant quartz. However, due to the low melting point of quartz relative to the temperature of basaltic lavas, it is possible emplacement of the overlying lava flow melted and incorporated any quartz that was previously present on the surface of the lower flow.

The percentages calculated above serve as a first order estimate than an exact percentage, especially given the complexity of the system and the challenges involved in pinpointing values for some endmembers. For example, loss of Nd from basalt during weathering would shift concentrations to lower values, causing an underestimation of input from ash/loess. For Sr, this shift to lower values could result in an overestimation of the marine aerosol endmember. Additionally, although mixing models have been calculated using pure ash or dust endmembers, it is likely that both are contributing in some proportion to the lower ¹⁴³Nd/¹⁴⁴Nd Cerro Colorado and Socavòn samples.

Eolian contributions into the Eastern Equatorial Pacific are less thoroughly characterized than for other parts of the Pacific Ocean. The primary studies have been by Nakai et al. (1993) and Xie and Marcantonio (2012) who disagree on the presence of dust from the northern hemisphere and Australia. The results of this research suggest that the dust and volcanic ash from the South American mainland can adequately explain Nd isotopic ratios in San Cristobal soil samples without input from Australia and the northern hemisphere.

6. Conclusions

The study sites on San Cristobal island can provide insight into how mineralogical controls on weathering may progress as climate changes, as well as how weathering in drier areas may progress with time. When age is held constant to examine the impact of climate, congruent weathering of olivine appears to dominate element retention in minimally weathered basalt in dry climates, with ferrihydrite formation and incongruent weathering of plagioclase playing a lesser role. As humidity and weathering intensity begin to increase, the importance of primary igneous minerals becomes secondary to the role of amorphous phases in controlling element retention. Crystalline secondary phases become important for a few elements, but do not become the dominant influence until conditions of high humidity and weathering intensity are reached. At this point, gibbsite, and to a lesser extent its amorphous precursors, become the dominant control on elemental retention with kaolin minerals and Fe oxides and oxyhydroxides and oxyhydroxides, and/or their amorphous precursors, become the dominant mineralogical control on element retention, with kaolin minerals playing a less significant role.

Radiogenic isotopic ratios indicate parent basalt weathering is not the only contributor to soils from the Socavòn site. ⁸⁷Sr/⁸⁸Sr ratios suggest the parent rock-derived Sr from the top 40 cm of the Socavòn site has been depleted by weathering and mostly replaced by marine aerosol isotopic compositions. ¹⁴³Nd/¹⁴⁴Nd isotopic compositions also suggest an eolian influence in the 160 cm sample from the Cerro Colorado site. Mixing models suggest Nd isotopic compositions of the Cerro Colorado sample can be explained by ~35% contribution from ash of similar composition to the pre-caldera phase of the Chacana volcano, and/or ~10% input from South American Eolian deposits. This suggests South American mainland sources alone can explain Nd isotope signatures in San Cristobal soils, without need for northern hemisphere and Australian dust deposition in the Eastern Equatorial Pacific.

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CHAPTER 4: IMPACT OF CLIMATE AND WEATHERING INTENSITY ON RARE EARTH ELEMENT DISTRIBUTION AND PEDOGENIC PROCESSES IN SOILS FROM SAN CRISTOBAL ISLAND, GALAPAGOS

1. Introduction

Understanding the Rare Earth Element (REE) content of soils has wide-ranging applications, from characterizing formation of hydrothermal ore deposits (Williams-Jones et al., 2012) to evaluating the suitability of proposed nuclear waste disposal sites (Coppin et al., 2002). Additionally, while REE were traditionally not viewed as critical for plant growth, research over the past ~20 years suggests low level additions of REE in soils promote plant growth and biomass production (Tyler, 2004; Hu et al., 2006; Laveuf and Cornu, 2009 and references therein). This has led to the use of REE fertilizers in some countries (Tyler, 2004a; Hu et al., 2006). Finally, in studies of soil formation, REE have proven to be valuable tracers of pedogenic processes due to their fractionation by weathering processes. REE pose and advantage over use of major elements since the same elements may be mobilized by multiple pedogenic processes (Laveuf and Cornu, 2009).

REE have similar chemical properties (Laveuf and Cornu, 2009) which result in similar behaviors in the environment (Tyler, 2004a). However, the decrease in ionic radii (Tyler, 2004a; Laveuf and Cornu, 2009) and increase in electronegativity from La to Lu, along with variations in coordination number (Laveuf and Cornu, 2009) results in subtle behavioral differences between the Light Rare Earth Elements (LREE; La to Eu) and the Heavy Rare Earth Elements (HREE; Gd to Lu). For example, HREE are more mobile than LREE (Nesbitt, 1979) because HREE form more stable complexes with colloids (Cantrell and Byrne, 1987; Kurtz et al., 2001; Laveuf and Cornu, 2009). Therefore, HREE are preferentially leached compared to LREE during weathering (Ma et al., 2002). In contrast, LREE are more soluble than HREE, meaning they are more likely to be present as free species (Laveuf and Cornu, 2009). These differences in LREE and HREE behavior produce the weathering-related fractionation that enables their use in deciphering pedogenic processes.

The dissolution of primary minerals releases REE into solution, where they can migrate into, out of, and throughout a weathering profile based on their relative mobility and solubility. Alternatively, some REE are retained in a weathering profile by incorporation into secondary minerals (Nesbitt, 1979; Braun et al., 1993). This incorporation can take to form of substitution for alkali metals and alkaline earths in some clay minerals (Laveuf and Cornu, 2009). However, adsorption is a more important REE-scavenging mechanism for both clay minerals (Coppin et al., 2002) and Fe oxides and oxyhydroxides (Pokrovsky et al., 2006). REE adsorption occurs because a negative surface charge exists on clay minerals and Fe- and Al-oxides and oxyhydroxides due to substitution of lower valence state elements (e.g., Coppin et al., 2002), or the non-stoichiometric substitution of Fe³⁺ for Al³⁺ (Li and Zhou, 2020). A second, more variable charge exists at the edges of clay mineral particles due to broken bonds (Coppin et al., 2002).

REE-fractionation by Fe oxides and oxyhydroxide adsorption has been debated in the literature (Laveuf and Cornu, 2009), with some studies noting an LREE-preference (e.g., Pokrovsky et al., 2006; Chang et al., 2016) while others indicate an HREE-preference (e.g., Land et al., 1999). In contrast, there is more agreement in the literature regarding REE fractionation by kaolinite and smectites. Coppin et al. (2002) noted a strong preference for HREE-adsorption onto kaolinite and smectites for solutions with high ionic strength and high Na concentration,

however, that preference was not present at lower ionic strengths. Yang et al. (2019) also noted an HREE preference for kaolinite and halloysite that was only present at high ionic strengths. Finally, organic matter impacts the distribution and transportation of REE (Aubert et al., 2004; Ma et al., 2007), with dissolved and colloidal forms tending to complex more stably with HREE (Cantrell and Byrne, 1987; Kurtz et al., 2001; Aubert et al., 2004; Laveuf and Cornu, 2009; Chang et al., 2016) while poorly biodegraded organic materials preferentially adsorb LREE (Land et al., 1999). Organic matter has abundant negatively charged surface groups (Tyler, 2004a) giving it a higher adsorption capacity than either kaolinite or goethite (Wu et al., 2001).

Ce and Eu are the only lanthanide elements that can occur in valence states other than 3+, and thus are well documented to behave differently than other REE. Ce anomalies form due to the impact of oxidation state on the mobility of Ce relative to its neighboring REE. Ce³⁺ is more mobile than Ce⁴⁺ (e.g., Banfield and Eggleton, 1989; Bau, 1999), and Ce³⁺ will be leached with other trivalent REE from reducing areas. However, if the REE-bearing solution interacts with an oxidizing area in a soil profile, Ce³⁺ can be oxidized to Ce⁴⁺ and precipitate from solution as insoluble CeO₂ (Braun et al., 1990; Ma et al., 2007). This precipitation of CeO₂ enriches Ce in the soil relative to trivalent REE, which causes a positive Ce anomaly in the soil and a negative Ce anomaly in the fluid. Additionally, oxidative scavenging by Mn (hydr)oxides and Fe oxyhydroxides can oxidize Ce^{3+} to Ce^{4+} , thereby retaining the Ce^{4+} while REE^{3+} are desorbed (Bau, 1999), Retention of immobile Ce⁴⁺ in oxidized soil during leaching of trivalent REE can form positive Ce anomalies (e.g., Patino et al., 2003 and references therein), and enhance them over time (Bau, 1999). In contrast, negative Ce anomalies are attributed to reducing conditions (Chapela Lara et al., 2018) and/or the transport and precipitation of Ce-depleted, REE³⁺-enriched fluids that have previously precipitated CeO₂ in more oxidized areas (Patino et al., 2003;

Babechuk et al., 2014). Eu can occur in a trivalent state like the other REE, but can also be found in a divalent form. Eu^{2+} can substitute for Ca^{2+} in plagioclase, which makes it the only REE influenced by plagioclase dissolution (Babechuk et al., 2014).

REE studies of pedogenic processes often focus on one profile (e.g., Braun et al., 1993; Land et al., 1999; Aubert et al., 2004; Ma et al., 2007; Berger et al., 2014; Janots et al., 2015; Jiang et al., 2018; Campodonico et al., 2019), although chrono sequences (e.g., Vermeire et al., 2016), and variations in lithology (e.g., Chapela Lara et al., 2018) have also been examined. However, the impact of climate and weathering intensity on REE distribution in soils, especially those developed on basaltic substrates, is significantly less studied. An improved understanding of how different extents of weathering and climate conditions impact REE distributions can aid understanding variations in pedogenic processes with climate. San Cristobal island in the Galapagos has relatively uniform basaltic parent rock with significant altitudinal-climate variations, however the distribution and systematics of REE in the soils and saprolites of the island have not been studied. This study aims to address the impact of climate and weathering intensity on the distribution of REE in San Cristobal research sites.

2. Geologic Setting and Samples

The geologic setting and sample descriptions are given in Section 2 of Chapter 2.

3. Methods

Dissolution protocol for Q-ICP-MS analysis of these samples is given in Section 3 of Chapter 2, with BHVO-2 and SBC-1 replicate analyses for Rare Earth Elements in Appendix Table A3.3a and b.

4. Results

Parent-composition-normalized REE patterns are shown for San Cristobal samples in Figure 4.1, while unnormalized data are presented in Table 4.1. For Socavòn, San Joaquin 2, San Joaquin 1, and El Junco samples, REE data are normalized to each site's respective rock sample, while Cerro Colorado samples are normalized to the average composition of the rocks from the other four sites. Variations in parent-normalized La/Lu ratios, Ce anomaly (Ce/Ce^{*}), and Eu anomaly (Eu/Eu^{*}) are shown with depth in Figures 4.2, 4.3, and 4.4 respectively. Ce/Ce^{*} is calculated as Ce/Ce^{*} = Ce_N/(Pr_{N²}/Nd_N) (Lawrence et al., 2006) where Ce, Pr, and Nd are all normalized to parent compositions. Europium anomaly (Eu/Eu^{*}) is calculated as Eu/Eu^{*} = Eu_N/(Sm_N x Gd_N)^{1/2} (Babechuk et al., 2014) where Eu, Sm, and Gd are also normalized to parent compositions.

Cerro Colorado soil and saprolite samples are enriched in all REE relative to the parent composition (Figure 4.1a), and also show HREE-enrichment relative to LREE content (Figures 4.1 and 4.2). This relative enrichment, as reflected in (La/Lu)_{Parent} ratios, are relatively consistent with depth (Figure 4.2). Most samples display a slightly negative Ce anomaly, except for 20 cm and 140 cm, which show a positive Ce anomaly (Figure 4.3). A negative Eu anomaly is also present in all samples (Figure 4.4).

San Joaquin 2 soil and saprolite samples are enriched in REE relative to the parent composition, except for the 100 cm sample which is depleted in most elements relative to the parent composition (Figure 4.1b). All samples are slightly depleted in LREE relative to HREE, with the exception of those from 0 cm, which is slightly LREE-enriched, and 140 cm which displays a relatively flat pattern. (La/Lu)_{Parent} values decrease sharply downward over the top 20 cm, then more gradually from 30 cm to 70 cm and 80 cm to 110 cm. Sample ratios increase



Figure 4.1. Parent rock normalized REE values for samples from a. Cerro Colorado, b. San Joaquin 2, c. Socavòn, and d. San Joaquin 1. See text for details

Table 4.1. Rare Earth Element Concentrations in Parts Per Million.

Sample														
Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cerro Co	lorado,	Dry Zor	ne											
CC-0	20.78	39.27	5.30	22.14	5.46	1.68	5.90	0.97	6.96	1.41	3.94	0.62	3.98	0.60
CC-10	19.20	38.79	5.18	21.48	5.25	1.61	5.77	0.96	6.74	1.38	3.95	0.64	4.04	0.63
CC-20	23.96	49.91	6.01	24.54	5.96	1.79	6.38	1.06	7.49	1.54	4.37	0.71	4.55	0.69
CC-40	19.11	38.13	5.14	21.12	5.20	1.57	5.50	0.92	6.18	1.27	3.75	0.59	3.80	0.59
CC-60	19.63	39.13	5.07	20.86	5.11	1.56	5.48	0.91	6.44	1.33	3.74	0.59	3.86	0.58
CC-80	21.20	41.72	5.64	23.07	5.49	1.70	5.96	1.00	6.52	1.34	4.01	0.61	3.94	0.64
CC-100	21.24	43.04	5.59	22.76	5.43	1.68	5.82	0.97	6.46	1.33	3.99	0.60	3.91	0.63
CC-120	20.04	40.97	5.26	21.36	5.20	1.56	5.39	0.91	6.30	1.27	3.60	0.56	3.63	0.57
CC-140	19.72	40.86	4.87	19.83	4.98	1.45	5.05	0.84	6.12	1.23	3.28	0.55	3.42	0.51
CC-160	19.09	38.37	5.09	20.76	5.13	1.53	5.35	0.90	6.20	1.24	3.55	0.56	3.53	0.55
Puerto Cl	hino, Dr	y Zone												
PC-R1	3.73	10.41	1.70	8.41	2.79	1.04	3.20	0.60	4.25	0.85	2.46	0.38	2.35	0.35
San Joaq	uin 2, Ti	ransition	n to H	umid Z	one									
SJ2-0	22.05	45.27	6.44	27.61	7.01	2.10	7.18	1.17	8.09	1.55	4.10	0.62	3.71	0.55
SJ2-10	17.74	37.09	5.63	24.70	6.34	2.15	6.68	1.12	7.41	1.44	4.04	0.59	3.67	0.55
SJ2-20	15.81	40.17	5.28	23.55	6.43	2.10	6.58	1.11	7.95	1.53	4.01	0.65	3.81	0.57
SJ2-30	16.88	36.38	5.54	24.05	6.27	2.15	6.41	1.08	7.56	1.50	3.99	0.63	3.89	0.57
SJ2-40	17.42	36.06	5.90	26.32	7.07	2.28	7.50	1.26	8.57	1.65	4.63	0.69	4.24	0.65
SJ2-50	17.80	37.97	6.13	27.06	7.33	2.41	7.46	1.27	8.37	1.64	4.68	0.69	4.33	0.66
SJ2-60	12.96	32.83	4.69	20.82	5.85	1.86	5.76	0.99	7.03	1.37	3.59	0.58	3.56	0.51
SJ2-70	11.68	27.94	4.22	18.54	5.09	1.72	5.31	0.94	6.43	1.24	3.50	0.55	3.38	0.51
SJ2-80	12.45	34.57	4.27	18.90	5.38	1.69	5.43	0.94	6.49	1.27	3.47	0.54	3.36	0.49
SJ2-90	11.83	42.83	4.20	18.36	5.03	1.73	5.14	0.88	5.95	1.12	3.16	0.48	3.09	0.46
SJ2-100	9.56	36.23	3.31	14.60	3.37	1.34	4.26	0.73	4.22	0.81	2.70	0.36	2.68	0.39
SJ2-110	11.38	37.08	4.03	17.94	5.18	1.72	5.28	0.92	6.35	1.23	3.43	0.54	3.38	0.51
SJ2-120	12.21	48.44	4.19	18.43	5.06	1.72	5.42	0.92	5.94	1.15	3.38	0.50	3.18	0.49
SJ2-130	15.00	41.81	4.94	21.53	5.74	1.85	6.05	1.02	6.49	1.27	3.67	0.53	3.36	0.52
SJ1-140	15.93	24.17	4.95	21.31	5.41	1.81	5.25	0.89	5.74	1.11	3.18	0.48	2.96	0.44
SJ2-150	14.68	35.16	5.16	22.58	6.16	2.05	6.01	1.03	6.66	1.28	3.66	0.55	3.51	0.52
SJ2-160	17.12	39.09	5.81	25.21	7.03	2.21	6.96	1.21	7.99	1.54	4.32	0.66	4.11	0.62
SJ2-170	17.77	43.85	5.87	25.69	6.93	2.21	6.98	1.18	7.92	1.55	4.20	0.65	3.95	0.59
SJ2-R2	12.42	26.58	3.81	16.58	4.33	1.46	4.51	0.75	5.18	1.01	2.69	0.41	2.48	0.36

Sample Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
San Joaquin 1, Humid Zone														
SJ1-0	28.73	53.43	6.09	20.27	3.75	0.97	2.96	0.41	2.41	0.40	1.11	0.17	1.20	0.17
SJ1-10	27.84	52.51	6.17	20.67	3.81	0.99	3.01	0.42	2.35	0.40	1.16	0.17	1.22	0.18
SJ1-20	31.20	59.32	6.82	23.04	4.27	1.13	3.40	0.47	2.63	0.44	1.28	0.19	1.35	0.20
SJ1-30	26.60	51.87	5.79	19.88	3.83	1.03	3.08	0.43	2.48	0.43	1.19	0.18	1.24	0.18
SJ1-40	25.52	50.38	5.86	20.48	4.12	1.13	3.39	0.49	2.89	0.50	1.35	0.21	1.36	0.20
SJ1-50	23.98	47.68	5.52	19.76	4.09	1.18	3.54	0.52	3.05	0.53	1.48	0.21	1.42	0.21
SJ1-60	21.70	44.70	5.07	18.72	4.07	1.21	3.66	0.55	3.40	0.61	1.64	0.24	1.47	0.22
SJ1-70	14.43	31.86	3.38	12.90	2.96	0.92	2.74	0.43	2.71	0.50	1.29	0.19	1.22	0.17
SJ1-80	11.13	26.93	2.72	10.79	2.67	0.88	2.57	0.43	2.77	0.53	1.52	0.24	1.56	0.24
SJ1-90	6.15	17.48	1.57	6.32	1.81	0.63	1.77	0.31	2.22	0.42	1.20	0.21	1.40	0.20
SJ1-100	13.84	114.76	3.57	13.66	3.66	1.16	4.02	0.65	4.30	0.82	2.41	0.38	2.28	0.33
SJ1-110	3.30	10.22	0.93	4.09	1.42	0.51	1.43	0.27	2.07	0.38	0.99	0.16	0.97	0.14
SJ1-120	2.70	16.09	0.84	3.76	1.42	0.50	1.49	0.28	2.10	0.41	1.12	0.19	1.17	0.16
SJ1-R1	26.25	52.72	6.39	25.16	6.04	1.70	5.98	1.00	6.75	1.36	3.82	0.61	3.79	0.57

Table 4.1. Rare Earth Element Concentrations in Parts Per Million, Continued.

Socavòn, Dry to Transition Zone

SV-0	21.24	49.37	5.75	23.79	5.94	1.92	6.32	1.02	6.84	1.32	3.53	0.53	3.27	0.46
SV-10	22.40	49.99	6.22	25.88	6.31	2.09	6.82	1.12	7.07	1.38	4.00	0.56	3.59	0.53
SV-20	16.02	41.93	4.83	20.24	5.17	1.70	5.45	0.92	6.13	1.19	3.32	0.50	3.11	0.45
SV-30	14.13	40.98	4.44	18.83	4.85	1.66	5.11	0.87	5.67	1.09	3.15	0.46	2.97	0.43
SV-40	13.63	48.27	3.99	16.76	4.30	1.42	4.22	0.70	4.67	0.90	2.46	0.37	2.37	0.34
SV-46	20.86	80.37	6.42	26.59	7.20	2.29	6.53	1.12	7.75	1.45	3.81	0.61	3.82	0.52
SV-R1	13.39	28.84	3.78	16.02	4.13	1.37	4.27	0.72	4.94	0.96	2.57	0.39	2.42	0.35

El Junco, Humid Zone

EJ-0	21.43	47.30	4.55	17.61	4.13	1.28	4.01	0.66	4.41	0.80	2.15	0.33	1.99	0.27
EJ-R1	13.16	27.64	3.46	14.46	3.65	1.24	3.82	0.64	4.35	0.85	2.30	0.35	2.14	0.31

again from 110 cm to 140 cm and from 150 cm to 170 cm (Figure 4.2). Samples from 80 cm to 130 cm show notable positive Ce anomalies, while the sample from 140 cm shows a strong
negative Ce anomaly (Figure 4.3). The San Joaquin 2 sample from 0 cm exhibits a notable negative Eu anomaly, while other samples range from slightly negative to slightly positive Eu anomalies (Figure 4.4).

Most San Joaquin 1 soil and saprolite samples are REE-depleted relative to the parent composition, except for samples from the top 20 cm which have slight enrichment in the lightest LREE relative to parent compositions (Figure 4.1d). Samples from the top 80 cm exhibit pronounced LREE-enrichment relative to HREE, while samples from below 80 cm exhibit LREE-depletion. (La/Lu)Parent values show a strong correlation with depth ($R^2 = 0.96$; Figure A4.1). Samples above 60 cm exhibit slightly negative Ce anomalies, while samples below 60 cm exhibit positive Ce anomalies that show an overall increase with depth (Figure 4.3). Samples from 100 cm and 120 cm show especially prominent positive Ce anomalies. Eu anomalies increase from very slightly positive near the surface to more strongly positive toward the bottom of the profile, with samples from 100 cm and 120 cm exhibiting notably less prominent anomalies that the neighboring samples (Figure 4.4).

The El Junco grab sample is enriched in LREE relative to the El Junco rock sample (Figure 4.1d). (La/Lu)_{Parent} ratios indicate this LREE-enrichment is greater than Cerro Colorado, San Joaquin 2, and Socavòn samples, but less than samples from the top 60 cm of San Joaquin 1 (Figure 4.2). The El Junco sample also has a positive Ce anomaly (Figure 4.3) and a very slightly negative Eu anomaly. (Figure 4.4)

Socavon soil and saprolite samples are enriched in REE relative to parent composition, except for the 40 cm sample which is slightly depleted in HREE (Figure 4.1c). All samples show to or significantly less than that from rainwater (Laveuf and Cornu, 2009). Waste disposal, such as sewage sludge, is also only a minor contributor resulting in only Eu and Sm enrichment











Figure 4.4. Variations in Eu anomaly versus depth for San Cristobal samples. Symbols are the same as in Figure 3.2. See text for details.

relatively flat REE patterns, with (La/Lu)_{Parent} values that decrease downward from the surface to 30 cm, before increasing again below 30 cm (Figure 4.2). Socavòn samples also show a positive Ce anomaly that increases with depth (Figure 4.3). Eu anomalies are minimal and trend from very slightly negative at the surface to very slightly positive at the bottom of the profile (Figure 4.4).

5. Discussion

5.1. Potential for Anthropogenic Impact on REE Concentrations of Soils

Potential anthropogenic inputs into soils include irrigation, fertilization, and waste disposal. Irrigation inputs are minor since REE concentrations of irrigation waters is comparable

(e.g., Zhang et al., 2001). Meanwhile, P-rich fertilizers, which are generally produced from REErich phosphates (Hu et al., 1998), can be an important source of REE in soils (Laveuf and Cornu, 2009). However, in non-polluted areas without major changes due to agricultural practices, REE input into soils should be primarily from parent materials.

Given the careful land management of the Galapagos islands, San Cristobal island is a relatively non-polluted environment. However, the enrichment of P in the San Joaquin 1 site (Figure 3.6d) and its location in an area that could be used for agriculture may suggest the presence of P-rich fertilizer or animal manure, which could impact REE content of the samples. To examine this possibility, REE values of phosphate fertilizer samples (Ramos et al., 2016) and manure samples (Hu et al., 1998) were normalized to the San Joaquin 1 rock compositions. The resulting REE patterns indicated flat LREE with steep HREE depletion for fertilizer (Figure 4.5). San Joaquin 1 samples exhibit relatively flat HREE patterns, suggesting the P addition was not from phosphate fertilizer. Pig and cattle manure sludge data from Hu et al. (1998) ranges from slightly HREE-depleted (cattle slurry) to slightly enriched (pig slurry; Figure 4.5). More importantly, the normalized REE values of the manure samples were approximately an order of magnitude less than those of the samples. Thus, manure sludge spreading, if occurring, is unlikely to influence REE values of San Joaquin samples.

The most likely scenario for the Galapagos soils may be wild animal manure. If REE concentrations in cattle and pig manure are similar to manure from wild animals on the island, then wild animal manure may explain how τ_P is enriched in the profile while τ_{REE} are depleted. The El Junco sample also indicates significant P-enrichment, that is also likely due to manure from wild animals, especially given the many birds that live around El Junco Lake. The El Junco

site is located in the Galapagos National Park near the only fresh water supply on the island. It is unlikely fertilizer is in use here. Thus, REE inputs into study sites are primarily from natural sources.



Figure 4.5. San Joaquin 1 rock normalized REE patterns for San Joaquin 1 samples, phosphate fertilizer, pig slurry, and cattle slurry. REE content of fertilizer from Ramos et al. (2016) and slurry from Hu et al. (1998). See text for details.

5.2 Potential Influence of Atmospheric REE Deposition

While REE content of parent rock has a significant impact on the REE concentrations in the resulting soil, it is not the only source. Nd isotopic ratios indicate the influence of volcanic ash on Socavòn samples (Figure 3.9a), which needs to be considered when interpreting REE in the profile. Some authors have noted striking similarities between soil and dust REE patterns (e.g., Kurtz et al., 2001), suggesting the eolian additions dominate the REE signals in their soil samples. However, the relatively flat REE patterns of the Socavòn profile do not resemble the more LREE-enriched volcanic ash patterns (Figure 4.6). Thus, it is likely the REE have been redistributed in the profile.



Figure 4.6 REE patterns for Ecuadorian volcanoes compared to those from the top 30 cm of the Socavòn profile. Ecuadorian volcano data are from Bryant et al. (2006) and Chiaradia et al. (2009). See text for details.

Given the complexities of lanthanide behavior as a series, the influence of the dust may be better seen through Y/Ho ratios. Y and Ho have nearly identical ionic radii, and thus exhibit very similar chemical behavior (Thompson et al., 2013). However, Y is slightly more mobile than Ho, and thus the two become increasingly fractionated with greater weathering intensity (Babechuk et al., 2015). Weathering indices are not reliable in highly weathered samples, however, depletion of the most mobile elements (Ca, Mg, Na, and Sr) is uniform throughout the profile and do not suggest substantial differences in weathering. Despite this, the 40 cm and 46 cm samples, which do not show a significant dust influence isotopically, have CHUR-normalized Y/Ho ratio of 0.64 and 0.60, respectively (Figure 4.7). In contrast, samples from the top 30 cm, which exhibit isotopic evidence of a dust influence, have upwardly increasing (Y/Ho)_{CHUR} ratios that range from 0.73 to 0.84. Thus, the two shallowest soil samples have (Y/Ho)_{CHUR} ratios identical to the unweathered Socavòn rock sample ((Y/Ho)_{CHUR} = 0.84) despite their high intensity of weathering.

An average (Y/Ho)_{CHUR} ratio of 1.1 was calculated for Ecuadorean volcanoes using data from Bryant et al. (2006) and Chiaradia et al. (2009). This suggests an ash component could be increasing the (Y/Ho)_{CHUR} values in the shallower Socavòn samples (Figure 4.7). The proportion Fe oxides and oxyhydroxides increases below 30 cm (Table 3.1), which can influence Y/Ho ratios by preferentially retaining Ho (Bau, 1999). Thus, the greater Fe oxide and oxyhydroxide content may contribute to the lower Y/Ho ratios in the bottom of the profile. However, Fe oxide and oxyhydroxide content does not explain the decrease in Y/Ho ratios with depth above 40 cm since the 20 and 30 cm samples have the profile's lowest percentage of Fe oxide and oxyhydroxides, or why the highest Y/Ho ratios occur in the top 10 cm of the profile. Given the mobility of HREE, samples from the lowest 6 cm of the profile may have also been impacted by redistribution of the dust signature, however, this impact is significantly less geochemically obvious than that observed in the upper 30 cm.

Nd isotope data were not collected for the San Joaquin 1 profile, and thus the profile was not evaluated for a dust signature in Chapter 2. San Joaquin 1 samples have steadily upward influence, however, the San Joaquin 1 profile only shows a slight increase in (Y/Ho)_{CHUR} ratios increasing (La/Lu)_{Parent} ratios, with values \geq 1.81 in the upper 70 cm. This could suggest an ash





above 100 cm and values are fairly consistent above 90 cm. Additionally, (Y/Ho)_{CHUR} ratios range from 0.48 to 0.60, which is significantly lower than the ash-influenced Socavòn samples. The higher fluid flux of the humid zone San Joaquin 1 profile could fractionate Y from Ho and thus obscure an ash component. However, the lack of cristobalite in San Joaquin 1 samples, suggests eolian ash deposition is not a significant contributor to the San Joaquin 1 profile. A similar lack of ash influence was noted in Nd isotopic data for samples from the San Joaquin 2 profile and could be due to the location of both sites on the leeward side of the island.

5.3 Models for REE Distribution in San Cristobal Soil Profiles

5.3.1 Cerro Colorado

REE patterns for most Cerro Colorado, San Joaquin 2, and Socavòn samples plot with normalized values >1, suggesting they are enriched relative to parent compositions (Figure 4.1a). However, the normalization of REE in a sample to REE in a parent does not account for volumetric changes that occur during weathering, and thus the observed enrichment in REE patterns could be due to decreased volume of the residue instead of REE addition to the system. τ_{REE} values, which are calculated using Nb as the immobile element, indicate that only the Cerro Colorado samples are actually enriched in all REE for all profile depths (Figure 4.8a).

Since the Cerro Colorado profile is relatively unweathered (Figure 4.8), transport of fluids into the profile from more altered areas may be responsible for the REE-enrichment. Patino et al. (2003) noted REE-enrichment in the least altered areas of corestones. They attributed this to influx of REE-rich fluids from more weathered areas, at which point leaching of elements such as Ca and Na increase the fluid's pH causing the REE to precipitate. REE can be mobile even during early stages of weathering (Banfield and Eggleton, 1989; Vermeire et al., 2016), however, the dry climate of the Cerro Colorado site likely aids in REE-retention. Additionally, the REE-enrichment may be aided by the presence of ferrihydrite, and the likely presence allophane, imogolite, and more amorphous ferrihydrite, which have larger cation-bonding surface areas than more crystalline alteration phases like kaolinite and gibbsite (Vitousek et al., 1997) and could serve as adsorption sites for the REE coming out of solution. Potential deposition by REE-enriched fluids is further supported by the greater enrichment of fluid-mobile HREE relative to LREE, as evidenced by TREE plots and (La/Lu)Parent < 1 (Figures 4.1 and 4.8).



←La ← Ce ━ Pr ★ Nd ← Sm ← Eu ᠊᠊ Gd ← Tb ★ Dy ● Ho ← Er ■ Tm ★ Yb ← Lu

Figure 4.8. Variations τ_{REE} values with depth for samples from a. Cerro Colorado, b. San Joaquin 2, c. Socavòn, and d. San Joaquin 1. See text for details

All Cerro Colorado samples exhibit a negative Eu anomaly (Figure 4.4), which could be caused by the high susceptibility of plagioclase to chemical weathering (Babechuk et al., 2014) given the abundant anorthite in the profile (Table 3.1). Weathering of plagioclase may preferentially leach Eu, resulting in a negative Eu anomaly in the residue (Laveuf and Cornu, 2009; Vermeire et al., 2016). A negative Eu anomaly due to Eu loss can occur during the early stages of weathering, as noted by Babechuk et al. (2014).

5.3.2 San Joaquin 2

Generally, REE retention decreases with increasing weathering intensity as is seen in the transition from the incipient weathered Cerro Colorado site to the moderately weathered San Joaquin 2 site (Figure 4.8 a and b). τ_{REE} values for San Joaquin 2 samples indicate they are enriched in most HREE at most profile depths, but LREE range from enriched in the top 50 cm to depleted (except for Ce) from 60 cm to 150 cm (Figure 4.8b). Given the presence of plagioclase at all depths in the profile (Table 3.1), the (Patino et al., 2003) REE precipitation model discussed above for the Cerro Colorado profile may also apply to San Joaquin 2 samples. Additionally, elevated Na concentrations in the fluid due to plagioclase leaching could result in Na adsorption onto kaolinite and halloysite. Higher density of sorbed Na can inhibit the adsorption of elements with larger ionic radii leading to preferential adsorption of HREE over LREE (Coppin et al., 2002; Yang et al., 2019). This mechanism may explain the greater enrichment of HREE relative to LREE in most San Joaquin 2 samples, especially given Yb and Lu, which have ionic radii comparable to Na, tend to be the most enriched HREE in the profile (Figure 4.8b).

REE distribution in soil portion of the San Joaquin 2 profile suggests some downward transport of REE, particularly HREE, may occur in the top 50 cm (Figure 4.8b). This downprofile redistribution appears limited to the soil and does not seem to impact the saprolite from 60 cm to 130 cm. REE content decreases between 130 cm and 140 cm (Figure 4.8b), corresponding to an increase in CIA value (Figure 3.4). As discussed in Chapter 3, the 140 cm and 150 cm interval may represent part of a soil horizon previously formed on an older flow. REE content increases from 140 cm to 170 cm, while CIA decreases over the same interval, suggesting the trend may be partially due to variations in weathering intensity. However, REEenrichment in the bottom 20 cm (Figure 4.8b), could suggest downward transportation of REE in the older soil has also occurred. Alternatively, the model proposed by Patino et al. (2003) for REE enrichment in less intensely weathered areas could be applicable in the lowest 30 cm, as discussed for higher in the profile.

San Joaquin 2 samples exhibit strong, positive Ce anomalies (Figure 4.3) and up to 54% Ce enrichment (Figure 4.8b) from 80 cm to 130 cm. This could be due to hot season storms temporarily raising the groundwater table, thus carrying oxygen to the middle portion of the profile (Ma et al., 2007). This effect may be especially prevalent during El Niño years, which can intensify the hot season storms (Trueman and D'Ozouville, 2010). Thus, REE-rich fluids migrating into the profile may have encountered water-table-induced oxidizing conditions in the middle of the profile and precipitated CeO₂. CeO₂ precipitation is preferred as the dominant mechanism over Ce adsorption because Ce anomaly does not correlate with and Fe oxide and oxyhydroxide content and/or kaolin mineral content. Underlying the 80 cm to 130 cm interval of positive anomalies is a negative Ce anomaly at 140 cm (Figure 4.3). TREE plots show Ce is the most depleted (33%) of any REE at 140 cm, while other REE show depletion ranging from 4%

to 19% (Figure 4.8b). Thus, the negative Ce anomaly at 140 cm may be inherited from the fluids that cause the positive Ce anomaly in the overlying portion of the profile.

Most San Joaquin 2 samples show an overall positive relationship between CIA and Eu anomaly, with samples exhibiting a negative anomaly having slightly higher CIA values than those with a positive anomaly. The exceptions to this are the samples from 0 cm, which exhibits a negative Eu anomaly despite a higher CIA values, and 100 cm, which exhibits a positive Eu anomaly despite relatively lower CIA values. Since the San Joaquin 2 profile also has plagioclase remaining, plagioclase leaching likely causes the Eu anomalies.

5.3.4 San Joaquin 1

 τ_{REE} values indicate that all San Joaquin 1 samples are REE-depleted and show greater HREE-depletion in the upper portion profile and greater LREE-depletion in the lower portion (Figure 4.8d). This preferential leaching of HREE at shallow depths has been frequently reported in the literature (e.g., Braun et al., 1990; Babechuk et al., 2014; Berger et al., 2014; Campodonico et al., 2019), and is probably due to the site's location in the humid zone causing greater flux of fluids through the profile. HREE form stronger complexes with Al-organic colloids, formed from the breakdown of plant material, and organo-mineral colloids. Thus the colloids could preferentially transport HREE down-profile in percolating fluids, while LREE are partially retained by adsorption onto mineral surfaces (Hu et al., 2006; Pokrovsky et al., 2006). In particular, a positive correlation ($\mathbb{R}^2 = 0.60$) exists between (La/Lu)_{Parent} and kaolin minerals (Figure A4.2a), that does not exist with Fe oxides and oxyhydroxides. This may suggest LREE remain adsorbed onto kaolin minerals, which are more abundant in the upper portion of the San Joaquin 1 profile, while HREE are leached. San Joaquin 1 samples also exhibit an inverse

correlation between (La/Lu)_{Parent} and gibbsite content ($R^2 = 0.73$; Figure A4.2b)). This suggests preferential adsorption of HREE onto gibbsite which is more abundant in the lower portion of the profile, possibly due to hydrolysis of kaolinite (Jiang et al., 2018) during seasonal shifts in the water table. Gibbsite may also form when Al from the Al-organic colloids precipitates out of solution (Hill et al., 2000).

In addition to producing colloids, the decomposition of organic material may cause less oxidizing conditions in the upper portion of the profile, enabling leaching of Ce to produce the observed depletion (Figure 4.8d). As the decomposition of organic material becomes less of an influence on oxidation state, Ce⁴⁺ is better retained relative to other LREE, resulting in a positive Ce anomaly (Figures 4.3 and 4.8d). When the fluid reaches the top of the saprolite, a drastic change in oxidation state may cause the precipitation of CeO₂, as reflected in the 112% Ce-enrichment at 100 cm and the strong positive Ce anomaly (Figure 4.3 and 4.8d). This drastic change in redox condition is likely due to seasonal fluctuations in the water table causing oxidizing conditions in the saprolite (Ma et al., 2007). The other prominent Ce anomaly at 120 cm may also be due to lower water table levels causing some CeO₂ precipitation, however the 70% depletion of Ce at this depth suggests that is a less frequent occurrence.

San Joaquin 1 samples show a positive correlation ($R^2 = 0.59$) between Eu anomaly and τ_{A1} values (Figure A4.3), and samples with Al loss have less positive Eu anomalies than those that are enriched in Al. This suggests Al retention may linked to Eu anomalies by adsorption of Eu onto Al-bearing phases. Without the anomalous samples at 100 cm and 120 cm, the R^2 value increases to 0.81 (Figure A4.3), suggesting Eu anomalies at 100 cm and 120 cm may be less linked to Al-retention than for the rest of the profile. San Joaquin 1 samples do not exhibit a

correlation between Eu anomaly and kaolin minerals and/or gibbsite, suggesting amorphous phases may play a significant role.

5.3.3 Socavòn

Socavòn REE patterns are enriched relative to parent compositions (Figure 4.1c), however, τ_{REE} indicate 12% to 36% depletion for Socavòn soil samples which range from, with only the saprolite sample (46 cm) having actual REE-enrichment (Figure 4.8c). Thus, except for Ce in some instances, the relative enrichment REE in Figure 4.1c is likely due to weatheringrelated volume loss instead of actual REE-enrichment relative to parent concentrations. The Socavòn profile is located in the dry to transition zone, however it is likely older than the other sites which accounts for the high weathering intensity of Socavòn samples.

The τ_{REE} values for Socavòn samples show the upper profile depletion and lower profile enrichment consistent with the downward transportation of REE by colloids in aqueous solution (Figure 4.8c). REE deposition in the upper saprolite may be due to adsorption onto Fe oxides and oxyhydroxides (Ma et al., 2007; Campodonico et al., 2019) which are most abundant at the bottom of the profile. However, the data suggest some complexities overlay this simple model. (La/Lu)Parent ratios progressively decrease with depth in the top 30 cm (Figure 4.2), which could be influenced by addition of an LREE-enriched South American ash component at the profile surface. The ash-derived LREE may be retained on mineral surfaces (Pokrovsky et al., 2006) or poorly-degraded organic phases (Land et al., 1999) in the top 10 cm, while the HREE, which more readily form aqueous complexes, are transported down profile. The ¹⁴³Nd/¹⁴⁴Nd ratios suggest the majority of ash-derived LREE redistribution is limited to the upper 30 cm of the profile. Thus, while down-profile transportation of parent-basalt-derived REE likely accounts for enrichment in the saprolite sample, the ash deposition was probably recent enough to not yet be fully redistributed. Although, REE redistribution may be relatively slow due to the dry to transition zone location of the Socavòn profile.

The positive Ce anomalies indicate oxidative conditions favored the presence of lessmobile Ce⁴⁺ throughout the profile (Figures 4.3 and 4.8c), however, τ_{Ce} values indicate up to 16% loss has occurred from the top 30 cm (Figure 4.8c). This is likely because the kinetics of Ce oxidation reactions are slower than those of REE³⁺ sorption/desorption reactions (Bau, 1999). Ce anomalies correlate positively with iron oxide and oxyhydroxide content (R² = 0.72; Figure A4.4) suggesting the Ce anomaly trend may be due in part to oxidative scavenging on the surfaces of Fe oxyhydroxides (Bau, 1999). In addition to oxidative scavenging, CeO₂ deposition may be necessary to account for the 91% enrichment observed in the saprolite sample (Figure 4.8c). The CeO₂ deposition may be explained downward-percolating fluids encountering significantly more oxidative conditions in the upper portion of the saprolite, possibly due to groundwater table fluctuations (Braun et al., 1990; Ma et al., 2007).

Socavòn samples exhibit a strong positive correlation between Eu anomaly and τ_{Al} values (R² = 0.92; Figure A4.3), with Al-loss corresponding to slightly negative Eu anomalies and Al gain to slightly positive Eu anomalies. However, Eu anomaly does not correlate with kaolin minerals, suggesting other Al phases exert the dominant influence Eu anomalies. This could suggest preferential transport of Eu by the Al-organic colloids discussed in Chapter 2, and/or Eu adsorption onto Al-rich amorphous phases, such as allophane, that may have precipitated from the Al-organic colloid-rich solution that percolated down profile.

5.4 Potential Impact of Climate and Weathering Intensity on REE Distribution and Pedogenic Processes

5.4.1 Variations Pedogenic Processes with Changing Climate

The San Cristobal profiles give insight into the impact of climate and weathering intensity on REE distribution, suggesting variations in these parameters may promote different dominant pedogenic processes, even in soils of comparable ages and substrates. These variations in pedogenic processes are summarized in Table 4.2. In dry conditions where weathering intensities are mild, pedogenic processes seem to revolve around aqueous transport of REEs into the system where they precipitate causing REE-enrichment. HREE are more enriched than LREE, and the flux of REE into the system is greater than the flux out of the system. Vertical transportation within the profile does not appear to influence REE distribution.

HREE-enrichment continues into seasonally humid conditions with moderate weathering, likely due to HREE-rich fluids from more weathered areas outside the profile. However, increased humidity and moderate extents of weathering begin to result in less LREE enrichment and locally LREE depletion. Additionally, REE enrichment at the soil-saprolite contact suggests downward transportation of elements is occurring within the soil. Deposition near the soilsaprolite interface of elements leached from higher in the profile has been reported in other moderately weathered sites (Aubert et al., 2004; Tyler, 2004b; Jiang et al., 2018). Additionally, seasonal fluctuations in the groundwater table may become important in producing positive Ce anomalies in seasonally humid conditions and/or moderate extents of weathering.

In high humidity zones, weathering is more intense and all REE are depleted. However, the more fluid-mobile HREE show greater depletion than LREE, as has also been noted in other

Climate:	Dry	Seasonally Humid	Humid	Older, Drier
Weathering Intensity:	Incipient	Moderate	High	High
t _{ree} :	HREE-enriched	HREE-enriched LREE-enriched &	HREE-depleted	HREE-depleted
	LKEE-enriched	depleted	LKEE-depieted	LKEE-depieted
REE Retention:	HREE > LREE	HREE > LREE	LREE > HREE	LREE > HREE
Dominant Pedogenic Proccesses:	REE-rich fluid influx	REE-rich fluid influx	Leaching	Leaching
	REE precipiation	REE precipiation	Down-profile HREE transportation	Down-profile HREE transportation
		Down-profile HREE transportation	T	
Dominant Minerals Controling REE:	Plagioclase dissolution	Plagioclase dissolution	LREE — Kaolinite + halloysite adsorption	REE adsorption onto Goethite + Hematite
		HREE — Kaolinite + halloysite adsorption	HREE — Gibbsite adsorption	
Ce Oxidation Mechanism:	N/A	Seasonal groundwater table fluctuations	Seasonal groundwater table fluctuations	Oxidative scavenging by Fe oxides and oxyhydroxides Seasonal groundwater table fluctuations
Eu Anomaly:	Plagioclase dissolution	Plagioclase dissolution	Adsorption onto Al phases, especially amorphous	Adsorption onto Al phases, especially amorphous

Table 4.2. Summary of pedogenic process and mineralogical controls on REE distribution under different climate conditions. See text for details.

highly weathered, high humidity locations by (e.g., Braun et al., 1990; Campodonico et al., 2019). In these systems, vertical redistribution and leaching of REE from the profile dominate.

The Socavòn profile suggests vertical redistribution and leaching of REE will eventually dominate even in drier settings, such as the lateritic profile from Madagascar in a study by Berger et al. (2014), but may require longer periods of time to develop. In these vertical-transport-dominated environments, translocation of REE can extend beyond the base of the soil and into the saprolite. This may be due to increased permeability at higher extents of weathering. Baker and Neill's (2017) study of saprolite formed on Columbia River Basalt notes that kaolinite becomes stable and feldspar disappears as saprolite permeability increases. Primary minerals in saprolite samples from both the Socavòn and San Joaquin 1 profiles have been replaced by kaolinite/halloysite + Fe oxides and oxyhydroxides ± gibbsite. The presence of amorphous and poorly crystalline phases is also suggested by broad peaks in the XRD analysis. This may indicate the permeability of highly weathered saprolite can be significant enough to allow some pedogenic processes to extend below the B/C horizon boundary. This enhanced permeability may aid seasonal water table fluctuations which may produce Ce anomalies, especially in more humid environments.

5.4.2 Variations in Mineralogical Controls of REE Distribution with Changing Climate

For samples of comparable age, differences in climate result in differences in weathering intensity as reflected by variations in profile mineralogy. This leads to variations in mineralogical controls on REE distribution under the different climatic conditions as summarized in Table 4.2. In dry to seasonally humid zones where primary minerals are still present, chemical weathering of plagioclase exerts the dominant control on observed REE patterns. As REE-rich fluids move from more weathered areas to less weathered areas, leaching of Ca and Na from plagioclase increases the fluid's pH causing REE to precipitate. This results in REE-enrichment, as proposed for corestones by Patino et al. (2003). Additionally, chemical weathering of plagioclase can influence fractionation of LREE from HREE in drier climate zones. Leaching elevates Na concentrations in the fluid which can result in Na adsorption onto kaolinite and halloysite. Higher density of sorbed Na can inhibit the adsorption of elements with larger ionic radii leading to preferential adsorption of HREE over LREE (Coppin et al., 2002; Yang et al., 2019). Finally, preferential leaching of plagioclase is the likely cause of negative Eu anomalies in the less weathered profiles of drier and seasonally humid areas. Alteration minerals seem to exert less influence on REE distribution, however, the presence of ferrihydrite, and possibly other amorphous phases, may also aid in REE-enrichment since they have larger cationbonding surface areas than more crystalline alteration phases (Vitousek et al., 1997).

As humidity and weathering intensity increase, primary minerals completely weather to kaolin minerals + Fe oxides and oxyhydroxides ± gibbsite, and thus alteration mineralogy becomes a significant control on REE distribution. In the highly weathered soils of humid climates, there seems to be a preference for LREE adsorption on kaolin minerals. This is the opposite of the less intensely weathered soils of drier climates, where HREE may be preferentially adsorbed onto kaolinite and halloysite. The difference could be due to the greater leaching of REE and Na in more humid climates, which would result in fluids with a lower ionic strength and very little Na to compete with REE for sorption sites. Thus, REE could be adsorbed as a group with no preference for HREE versus LREE (Coppin et al., 2002). However, the greater flux of water in wetter climates would preferentially desorb HREE to form colloidal complexes, leading to relative LREE-enrichment in the REE that remain. In contrast, HREE

appear to preferentially adsorb onto gibbsite. This may result from the preferential transport of HREE by Al-colloids, with the eventual break down of the colloids releasing Al that could then precipitate out of solution as gibbsite. Meanwhile, Al-bearing phases especially amorphous ones, may preferentially retain Eu relative to other LREE, producing a positive Eu anomaly in some soils of humid climates.

The discussion above examines the impact of changing climate on samples of similar age. However, in older, drier areas, primary minerals are eventually lost and secondary minerals exert significant influence on REE patterns. In particular, oxidative scavenging by Fe oxides and hydroxides may influence Ce anomalies by oxidizing Ce³⁺ to Ce⁴⁺, thereby retaining the Ce⁴⁺ while REE³⁺ are desorbed (Bau, 1999), Retention of immobile Ce⁴⁺ in oxidized soil during leaching of trivalent REE can form positive Ce anomalies (e.g., Patino et al., 2003 and references therein), and enhance them over time (Bau, 1999). Additionally, a combination of Al-rich phases such as kaolin minerals and allophane seem to influence Eu anomalies, likely by preferential adsorption of Eu over other LREE.

6. Conclusions

San Cristobal samples from different climate zones provide insight into the impact of changing climate on REE distribution in samples of similar age and substrates. Variations in climate and weathering intensity seem to promote different dominant pedogenic processes which redistribute REE. Overall, REE content decreases with increasing humidity and weathering intensity. In dry to seasonally humid climates where primary plagioclase is present, the flux of HREE into the profile is significantly greater than leaching of HREE from the profile resulting in HREE-enrichment. LREE-enrichment is also noted under dry conditions with mild weathering

but lessens under increased humidity and moderate weathering intensity such as observed at the San Joaquin 2 site. As humidity and weathering intensity increase, vertical translocation of elements within the profile becomes a significant pedogenic process, and the leaching ultimately outweighs the influx of REE into the profile. Under these conditions, all REE are depleted, with HREE more depleted than LREE. Additionally, seasonal fluctuations in the groundwater table become important in creating positive Ce anomalies as humidity and weathering intensity increase.

Mineralogically, chemical weathering of plagioclase plays the dominant role in dry to seasonally humid climates where primary minerals are still present in soil. Elevated Na and Ca in fluids leaching plagioclase can promote precipitation of REE transported into the profile by aqueous solutions from more weathered areas, while elevated Na can also induce an HREE adsorption preference for kaolinite and halloysite. Additionally, preferential leaching of Eu from plagioclase may result in negative Eu anomalies in drier climates. In more humid climates where primary minerals have been depleted, kaolin minerals may preferentially retain LREE, while HREE favor adsorption onto Gibbsite. Meanwhile, preferential retention of Eu by adsorption onto Al-bearing phases may produce Eu anomalies.

The Socavon profile gives insight into how pedogenic processes and mineralogy may influence REE distribution in older soils from drier climates, suggesting leaching and vertical translocation of REE will eventually become significant even though they may take longer to develop. As with highly weathered profiles from humid climates, Eu anomalies appear to be related to preferential Eu adsorption onto aluminous phases. Additionally, water table fluctuations combined with oxidative scavenging of Ce by Fe oxides and oxyhydroxides may be responsible for positive Ce anomalies in older, drier conditions.

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APPENDIX 1: COMPILATION OF PREVIOUSLY PUBLISHED DATA FOR ALEUTIAN SAMPLES

 Table A1.1. Compiled Major Element Data for Aleutian Lavas

Sample #	Latitude (N)	Longitude (W)	Lithology	SiO ₂ ^a	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Mount Wes	tdahl, Unin	nak Island												
SAR11	54.556	164.761	Basaltic andesite	51.96	1.59	16.76	11.15	0.17	4.03	9.12	3.79	0.95	0.24	99.76
SAR4	54.556	164.761	Trachy- dacite	63.85	1.23	16.21	6.58	0.09	1.65	4.07	5.65	1.90	0.39	101.62
Bogoslof Is	land													
1927	53.930	168.030	Basalt	46.00	1.40	18.50	10.49	0.17	5.40	11.90	2.60	1.60	0.36	99.03
Mount Okn	nok, Umnak	c Island												
UM10	53.420	168.130	Basalt	51.30	0.68	16.20	8.30	0.12	7.45	11.32	2.08	0.61	0.13	98.19
UM11	53.420	168.130	Basaltic andesite	52.00	0.76	17.45	8.75	0.17	6.60	10.99	2.38	0.75	0.15	
UM22	53.420	168.130	Basalt	51.28	1.06	18.36	8.70	0.14	4.91	11.17	2.73	0.53		98.88
UM4	53.420	168.130	Basalt	51.70	1.12	17.70	8.92	0.14	5.45	10.12	3.07	0.97	0.20	99.39
UM5	53.420	168.130	Basaltic andesite	53.60	1.30	16.50	11.20	0.17	4.46	9.17	3.59	0.77	0.18	100.94
UM16	53.420	168.130	Basaltic andesite	53.83	1.81	15.17	11.61	0.19	4.14	7.92	3.37	1.19	0.06	99.29
QAF-70	53.420	168.130	Basalt	51.35	1.03	17.71	9.45	0.18	5.13	10.71	2.86	0.66	0.16	100.29

Sample #	Latitude (N)	Longitude (W)	Lithology	SiO ₂ ^a	TiO ₂	Al_2O_3	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total
Mount Rec	heshnoi, Un	nnak Island												
LUM-17	53.367	169.183	Andesite	57.82	0.85	17.74	6.47	0.12	3.98	7.45	3.31	1.33	0.15	99.94
LUM-21	53.583	169.283	Basalt	50.07	0.72	15.92	8.15	0.15	10.10	10.12	2.35	0.86	0.13	99.48
Islands of F	our Mounta	ains												
FMI-8	53.070	169.770	Andesite	60.25	0.57	18.01	5.82	0.09	2.35	6.16	4.23	1.78	0.17	99.43
FMI-7	52.900	170.050	Andesite	59.37	0.77	17.44	6.37	0.09	3.58	7.10	3.83	1.09	0.12	99.77
FMI-6	52.820	169.950	Rhyolite	70.08	0.62	15.00	4.01	0.06	0.94	3.13	4.53	2.69	0.12	101.18
FMI-5	52.750	170.120	Andesite	59.58	0.88	18.39	6.47	0.10	2.08	7.40	4.11	0.82	0.15	99.95
Yunaska Isl	and													
FMI-2	52.650	170.760	Andesite	63.00	1.09	16.39	6.61	0.10	2.09	5.59	5.49	1.13	0.18	101.67
Great Sitkin	n Volcano, (Great Sitkin I	sland											
SIT-RK4	52.080	176.130	Trachy- dacite	65.90	0.49	16.85	4.34	0.15	1.20	3.48	5.20	2.59	0.17	100.23
GS721B	52.080	176.130	Andesite	59.88	0.76	16.76	7.55	0.11	3.25	7.32	3.86	1.31		100.80
GS723	52.080	176.130	Andesite	61.21	0.65	17.20	6.48	0.09	2.62	6.37	4.01	1.41		100.04
GS727	52.080	176.130	Basalt	49.68	0.85	19.39	9.33	0.14	5.60	10.97	2.66	0.82		99.44

 Table A1.1. Compiled Major Element Data for Aleutian Lavas, Continued.

Sample #	Latitude (N)	Longitude (W)	Lithology	SiO ₂ ^a	TiO ₂	Al_2O_3	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total
Mount Ada	gdak, Adak	Island												
ADG14	51.9898	176.5871	Basalt	48.62	0.99	18.71	10.27	0.15	5.68	11.52	2.75	1.05	0.21	99.95
ADG2	51.9898	176.5871	Andesite	57.49	0.49	19.33	6.75	0.11	2.44	8.16	3.58	1.02	0.21	99.56
ADG7A	51.9898	176.5871	Basalt	50.79	0.91	19.10	9.62	0.15	4.79	10.24	2.83	0.97	0.20	99.60
ADG8	51.9898	176.5871	Andesite	60.96	0.48	17.43	6.00	0.10	2.53	7.17	3.74	1.09	0.17	99.67
Mount Mof	fett, Adak I	Island												
MOF81-17	51.930	176.750	Basaltic andesite	52.96	0.74	18.83	8.68	0.13	4.19	9.94	3.30	1.17	0.22	100.14
MOF81- 56A	51.930	176.750	Andesite	62.57	0.55	17.52	5.13	0.08	2.07	6.38	3.68	1.65	0.20	99.83
MOF81-15	51.930	176.750	Basalt	49.35	0.86	18.57	9.52	0.15	4.84	10.80	2.85	1.11	0.15	98.20
MOF81-44	51.930	176.750	Andesite	57.36	0.62	17.50	6.91	0.11	3.58	8.42	3.55	1.57	0.15	99.77
MOF53A (ADK-53)	51.930	176.750	High-Mg andesite	55.50	0.86	15.50	6.21	0.10	5.58	9.51	2.98	1.47	0.32	98.03
Bobrof Isla	nd													
BO9-6A	51.900	177.430	Andesite	62.00	0.56	17.69	5.43	0.09	2.77	6.96	3.82	1.32	0.17	100.81
BO9-8A	51.900	177.430	Basaltic andesite	53.73	0.69	20.34	7.63	0.13	3.24	10.13	2.85	0.84	0.55	100.13

 Table A1.1. Compiled Major Element Data for Aleutian Lavas, Continued.

Sample #	Latitude (N)	Longitude (W)	Lithology	SiO ₂ ^a	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total
Buldir Islar	nd													
BUL4D	52.370	184.020	Basaltic andesite	55.90	0.74	17.57	6.69	0.11	5.75	8.31	2.76	0.96	0.07	98.86
BUL6A	52.370	184.020	Andesite	61.49	0.49	17.53	4.75	0.09	3.72	6.46	3.66	1.50	0.13	99.82
BUL6B	52.370	184.020	Basaltic andesite	52.66	0.65	18.31	6.78	0.12	7.35	8.78	3.34	0.81	0.14	98.94

Table A1.1. Compiled Major Element Data for Aleutian Lavas, Continued.

^aMajor element concentrations for all elements from Kay and Kay (1994) and references therein, except for 1927, QAF-70, LUM-17, and LUM-21 from Class et al. (2000).

Sample #	Li	$\mathbf{Sr}^{\mathbf{b}}$	Y	Cs	Ba	La	Nd	Yb	Th
Mount Westdahl,	Unimak Islar	nd							
SAR11	7.07	336	29.6	0.88	326	10.6	15.7	2.78	1.78
SAR4	18.26	286	38.4	1.69	537	17.8	24.4	3.72	3.32
Bogoslof Island									
1927 ^a	5.00	822	22.5	1.40	816	14.1	24.8	2.03	3.16
Mount Okmok, U	mnak Island								
UM10	4.83	562	13.7	0.24	196	6.1	8.7	1.25	1.54
UM11	4.79	622	16.9	0.38	219	7.4	10.8	1.60	1.65
UM22	6.09	264	39.5	2.51	475	15.3	20.8	3.90	3.08
UM4	5.57	368	36.3	0.91	373	12.1	17.6	3.40	2.74
UM5	11.83	290	22.8	1.21	271	7.9	11.2	2.17	1.50
UM16	10.08	362	39.0	1.77	403	12.8	18.8	3.69	2.87
QAF-70 ^a	9.79	361	21.1	0.88	224	6.26	10.22	2.08	1.23

Table A1.2. Compiled Trace Element Data for Aleutian Lavas

Sample #	Li	Sr ^b	Y	Cs	Ba	La	Nd	Yb	Th
Mount Recheshne	oi, Umnak Isla	and							
LUM-17 ^a	22.57	354	18.8	1.43	447	9.63	12.01	1.83	3.15
LUM-21 ^a	9.22	521	13.9	0.51	237	6.93	10.09	1.34	1.41
Islands of Four M	Iountains								
FMI-8	11.57	593	15.4	1.12	559	17.1	15.7	1.52	2.67
FMI-7	12.67	252	16.7	0.38	319	6.8	8.4	1.71	1.24
FMI-6	16.49	135	21.5	3.19	516	9.6	11.6	2.20	4.06
FMI-5	8.45	234	20.9	0.36	264	6.0	8.9	2.07	1.05
Yunaska Island									
FMI-2	13.56	213	24.9	0.27	318	8.2	11.3	2.45	1.50
Great Sitkin Volc	ano, Great Sit	tkin Island							
SIT-RK4	16.30	255		1.28	935	14.6	18.3	3.42	5.26
GS721B	11.13	285	20.1	1.65	331	7.0	9.7	2.03	1.70
GS723	13.50	285	22.2	0.67	407	8.2	11.5	2.31	2.26
GS727	7.93	381	15.3	0.41	209	5.3	8.2	1.44	0.92

Table A1.2. Compiled Trace Element Data for Aleutian Lavas, Continued

Sample #	Li	$\mathbf{Sr}^{\mathbf{b}}$	Y	Cs	Ba	La	Nd	Yb	Th
Mount Adagdak, A	Adak Island								
ADG14	10.79			0.36	441	8.44	11.64	1.94	2.08
ADG2	10.78	408		1.14	453	9.85	12.6	2.08	2.44
ADG7A	5.23	472		1.18	406	7.8	13.5	1.86	1.94
ADG8	9.48	396		2.83	528	11.1	12.6	1.94	3.04
Mount Moffett, A	dak Island								
MOF81-17	5.83	550	17.7	1.45	470	9.2	12.1	1.70	2.66
MOF81-56A	9.37	328	12.4	1.18	586	9.4	9.4	1.36	3.41
MOF81-15	5.73	610	16.8	0.40	344	7.6	11.4	1.52	1.84
MOF81-44	9.12	374	15.0	0.90	514	8.9	9.8	1.53	2.94
MOF53A (ADK-53)	7.20	1783	16.3	0.24	536	29.15	34.06	0.94	3
Bobrof Island									
BO9-6A	9.92	493	18.3	2.03	688	14.1	16.1	1.93	4.26
BO9-8A	6.69	524	19.7	1.58	424	9.8	14.6	2.11	2.65

|--|

Sample #	Li	Sr	Y	Cs	Ba	La	Nd	Yb	Th
Buldir Island									
BUL4D	12.75	436	12.3	1.04	298	8.5	10.5	1.12	1.98
BUL6A	13.80	400	10.6	3.28	367	9.3	9.9	0.97	2.40
BUL6B	7.24	354	16.3	0.34	236	6.6	10.4	1.52	1.00

Table A1.2. Compiled Trace Element Data for Aleutian Lavas, Continued

^aLi concentrations from Tomascak et al. (2002). Li concentrations for all other samples are from this study.

^bTrace element data other than Li are from Yogodzinski et al. (2015), except for SIT-RK4 and Mount Adagdak samples from Kay and Kay (1994); and 1927, QAF-70, LUM-17, and LUM-21 from Class et al. (2000). Y concentration for MOF53A is from Walker (1974) and Pb concentration is from Sun (1980).

Sample #	δ ⁷ Li	$\delta^{18}O^{b}$	¹⁴³ Nd/ ¹⁴⁴ Nd ^c	¹⁷⁶ Hf/ ¹⁷⁷ Hf ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ^d	Chemical Index of Alteration ^e	Mafic Index of Alteration ^f
Mount Westda	ahl, Uni	mak Isla	and						
SAR11	2.2	6.2	0.513073	0.283154	18.867	15.563	38.403	41.28	42.02
SAR4	2.4	6.4	0.513076	0.283148	18.859	15.561	38.388	46.37	47.66
Bogoslof Isla	nd								
1927 ^a	2.3	5.6	0.513045	0.283108	18.748	15.552	38.229	40.09	38.58
Mount Okmo	k, Umn	ak Island	1						
UM10	4.1	5.7	0.513032	0.283153	18.726	15.545	38.245	39.64	33.67
UM11	5.7		0.513037	0.283153				41.39	36.36
UM22	3.0	4.6	0.513046	0.283154	18.916	15.602	38.513	41.98	39.36
UM4	4.6	6.0	0.513054	0.283149	18.659	15.515	38.127	41.94	38.56
UM5	3.6	5.1	0.513042	0.283142	18.887	15.570	38.430	41.34	41.34
UM16	3.3		0.513061	0.283151	18.906	15.592	38.489	41.67	42.47
QAF-70 ^a	2.8		0.513026		18.861	15.557	38.372	41.57	39.20

 Table A1.3. Compiled Isotope and Alteration Index Data for Aleutian Lavas

Sample #	δ ⁷ Li	$\delta^{18}O^{b}$	143 Nd/ 144 Nd ^c	¹⁷⁶ Hf/ ¹⁷⁷ Hf ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ^d	Chemical Index of Alteration ^e	Mafic Index of Alteration ^f
Mount Reche	shnoi, U	Jmnak Is	sland						
LUM-17 ^a	3.9		0.512954		18.984	15.597	38.568	46.48	42.27
LUM-21 ^a	3.2		0.51303		18.677	15.524	38.130	40.70	30.81
Islands of Fo	ur Mour	tains							
FMI-8	2.9	5.9	0.513063	0.283159	18.6444	15.5327	38.1544	47.28	45.96
FMI-7	2.5	6.6	0.513058	0.283169				46.10	42.72
FMI-6	2.4	7.2	0.513036	0.283148	18.8860	15.5808	38.4548	48.30	49.19
FMI-5	8.4	6.5	0.513003	0.283128	18.9615	15.5903	38.536	46.56	46.57
Yunaska Islar	nd								
FMI-2	3.6	5.3	0.513023	0.283141	18.8869	15.5757	38.4436	44.53	45.06
Great Sitkin V	Volcano,	Great S	itkin Island						
SIT-RK4	5.6	6.5	0.513023	0.283155	18.8482	15.5785	38.4320	48.79	49.03
GS721B	2.7	5.6	0.513048	0.283187	18.8591	15.5768	38.4357	44.30	43.02
GS723	5.1	6.6	0.513042	0.283192				46.61	45.29
GS727	-0.7		0.51305	0.283175	18.7405	15.5535	38.2879	43.48	39.78

Table A1.3. Compiled Isotope and Alteration Index Data for Aleutian Lavas, Continued
Sample #	δ ⁷ Li	$\delta^{18}O^{b}$	$^{143}\mathrm{Nd}/^{144}\mathrm{Nd^{c}}$	¹⁷⁶ Hf/ ¹⁷⁷ Hf ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ^d	Chemical Index of Alteration ^e	Mafic Index of Alteration ^f
Mount Adagda	ak, Ada	ık Island							
ADG14	0.5							41.29	38.82
ADG2	2.1	5.9						46.96	46.28
ADG7A	1.6	6.2						43.99	41.57
ADG8	4.7							46.11	44.76
Mount Moffet	t, Adak	Island							
MOF81-17	5.1	6.1	0.513008	0.283161				43.19	41.40
MOF81-56A	1.8		0.513026	0.283167				47.40	46.16
MOF81-15	1.8	5.8	0.512998	0.28315				42.11	40.14
MOF81-44	3.8	6.0	0.513019	0.283171	18.8120	15.5718	38.3939	43.37	41.25
MOF53A (ADK-53)	3.7	7.5	0.513089	0.283205	18.462	15.499	37.964	39.46	34.44
Bobrof Island									
BO9-6A	4.1	6.9	0.513043	0.2831745	18.7770	15.5621	38.3408	46.48	44.04
BO9-8A	3.1	5.5	0.513047	0.283182	18.8011	15.5648	38.3670	45.86	44.43

Table A1.3. Compiled Isotope and Alteration Index Data for Aleutian Lavas, Continued

Table A1.3. Compiled Isotope and Alteration Index Data for Aleutian Lavas, Continued

Sample #	δ ⁷ Li	$\delta^{18}O^{b}$	$^{143}Nd/^{144}Nd^{c}$	¹⁷⁶ Hf/ ¹⁷⁷ Hf ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ^d	Chemical Index of Alteration ^e	Mafic Index of Alteration ^f
Buldir Island									
BUL4D	2.7	7.4	0.5130665	0.283173	18.6110	15.480	38.054	45.92	38.78
BUL6A	4.3	7.1	0.513081	0.283182	18.6410	15.514	38.132	47.48	42.05
BUL6B	5.5	5.7	0.513089	0.283187	18.5650	15.486	38.028	45.05	36.10

 $^{a}\delta^{7}$ Li values from Tomascak et al. (2002). δ 7Li values for all other samples are from this study.

 ${}^{b}\delta^{18}O$ values are from Kay and Kay (1994) and references therein.

^cNd and Hf isotope ratios from Yogodzinski et al (2010) except for 1927, QAF-70, LUM-17, and LUM-21 from Class et al. (2000); and MOF53A from Munker et al. (2004).

^dPb isotopes from Yogodzinski et al. (2015) and references therein, except for SAR11, SAR4, UM10, UM5 from Nielsen et al. (2016); 1927, QAF-70, LUM-17, and LUM-21 from Class et al. (2000); and MOF53A from Sun (1980).

^eChemical Index of Alteration calculated using equation of Nesbitt and Young (1982).

^fMafic Index of Alteration calculated using equation of Babechuk et al. (2014)

Sample #	Latitude (N)	Longitude (W)	Lithology	${\rm SiO_2}^{\rm a}$	TiO ₂	Al_2O_3	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total
Hidden Bay	y pluton, A	dak Island.												
HB5-137	51.695	176.717	Silicic Granodiorite	67.01	0.61	16.33	3.42	0.05	1.64	4.28	3.89	2.58	0.18	99.99
HB5-193	51.710	176.622	Diorite	58.88	0.93	17.18	6.00	0.11	3.53	6.31	3.77	3.06	0.24	100.00
HB7-10	51.724	176.714	Gabbro	50.64	0.92	17.16	8.62	0.16	7.59	10.95	2.90	0.89	0.18	100.00
BW7-28	51.695	176.717	Feldspar Porphyry	60.37	1.13	17.38	6.23	0.14	1.77	4.62	4.68	3.28	0.41	100.00
HB5-160	51.723	176.632	Diorite	53.47	1.65	18.70	7.96	0.13	4.34	8.39	3.65	1.14	0.57	100.00
HB7-16	51.718	176.693	Porphyric Diorite	53.77	0.74	17.65	7.79	0.15	5.97	9.73	2.95	1.10	0.16	100.00
Mafic dyke	e cutting H	idden Bay pl	uton and older	host rocl	k									
BW8-55	51.695	176.717	Dike	49.54	1.17	17.55	8.95	0.18	8.13	10.82	2.77	0.54	0.21	99.86
HB6-83J	51.718	176.653	Dike	54.75	0.73	16.37	8.18	0.19	7.36	8.07	3.16	0.87	0.31	99.97
Finger Bay	pluton, Ac	lak Island												
FB53	51.831	176.588	Gabbro	48.49	0.91	19.86	8.48	0.13	4.86	12.82	2.66	0.81	0.18	99.20
FB44	51.831	176.588	Gabbro	51.06	1.1	17.34	10.09	0.19	4.77	10.6	3.06	1.25	0.21	99.67
FB97	51.831	176.588	Gabbro	50.72	0.95	19.10	9.54	0.22	4.24	9.87	3.79	1.38	0.3	100.11

 Table A1.4. Compiled Major Element Data for Aleutian Intrusions

Table A1.4. Com	piled Major	Element Data	for Aleutian	Intrusions,	Continued

Sample #	Latitude (N)	Longitude (W)	Lithology	SiO ₂ ^a	TiO ₂	Al_2O_3	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total
Kagalaska pluton, Kagalaska Island														
KAG7-50	51.829	176.429	Gabbro	51.50	0.95	20.19	8.51	0.16	2.96	9.46	4.10	1.47	0.71	100.00
KAG7-32	51.808	176.437	Granodiorite	66.05	0.43	16.35	3.44	0.06	2.08	4.67	4.13	2.64	0.14	100.00
KAG7-1A	51.818	176.431	Granodiorite	63.14	0.66	17.82	3.98	0.15	2.40	5.34	4.18	2.17	0.17	100.00
KAG7-19B	51.837	176.438	Mafic Granodiorite	58.47	1.19	16.66	7.15	0.24	3.32	6.06	4.03	2.58	0.30	100.00
KAG7-44	51.833	176.456	Basaltic Dike				12.68				2.28			
Unknown g	geologic co	ontext, Great	Sitkin Island											
GS725B	52.080	176.130	Gabbro xenolith	52.39	0.89	18.62	9.08	0.14	4.14	9.72	3.12	1.10		99.20
9 3 / (. 1	TZ / 1	(2010)			C ''	(1000)		1	07.0	17	1 17	(1004)	

^aMajor element data from Kay et al. (2019) except for BW8-55 from Citron (1980); FB53 and FB97 from Kay and Kay (1994); FB44 from Kay et al. (1983); and GS725B from Neuweld (1987)

Sample #	Li	Sr ^a	Y	Cs	Ba	La	Nd	Yb	Th	δ7Li	¹⁴³ Nd/ ¹⁴⁴ Nd ^b	Chemical Index of Alteration ^c	Mafic Index of Alteration ^d
Hidden Bay	pluton, A	Adak Isl	and										
HB5-137	5.34	601	40.0	0.22	1026	14.20	17.1	1.42	5.21	7.7	0.513032	49.03	47.03
HB5-193	12.99	512	21.9	1.16	562	19.2	23.0	2.03	4.40	2.3		45.03	41.76
HB7-10	9.20	689	16.1	1.08	173	7.51	12.31	1.56	0.86	4.7	0.513100	40.10	34.17
BW7-28	15.19	609	63.0	1.02	857	26.37	39.8	4.28	4.64	2.7		46.94	47.47
HB5-160	8.17	679	23.0	0.61	243	15.56	24.0	2.07	2.06	4.4	0.513053	45.40	42.11
HB7-16	5.69	1068	11.1	0.37	244	8.80	12.5	0.99	1.40	5.1	0.513062	42.65	37.37
Mafic dyke	cutting H	lidden E	Bay plu	ton and	dolder	host roc	k						
BW8-55	18.52	632	22.0		205	10.8		1.61		2.4	0.513074	41.43	34.50
HB6-83J	10.60	687	18.0	0.63	303	20.51	28.98	1.50	2.96	7.2	0.513051	44.03	36.00
Finger Bay p	pluton, A	dak Isla	ind										
FB53	2.95	728	13.0	0.32	233	7.7	15.3	1.30	1.47	3.2	0.513101	41.01	38.78
FB44	3.12	743	13.0		359	10.0	15.0	1.77	1.68	5.9		40.33	39.37
FB97	9.50	753	18	0.73	329	10.1	16.5	1.60	1.60	0.7	0.513095	42.66	41.54

Table A1.5. Compiled Trace Element, Isotope, and Weathering Index data for Aleutian Intrusions

Sample #	Li	Sr ^a	Y	Cs	Ba	La	Nd	Yb	Th	δ7Li	¹⁴³ Nd/ ¹⁴⁴ Nd ^b	Chemical Index of Alteration ^c	Mafic Index of Alteration ^d
Kagalaska p	luton, K	agalaska	a Islano	d									
KAG7-50	2.20	1000	22.0	0.71	328	13.40	22.51	1.614	1.75	4.3	0.513058	44.16	44.28
KAG7-32	6.83	463.3		0.94	562	10.0	9.58	0.98	2.87	3.8	0.513072	47.38	44.53
KAG7-1A	8.34	757	14.0	0.57	352	9.6	13.6	0.97	1.92	6.9		48.51	45.25
KAG7-19B	9.54	574	31.0	1.37	539	20.9	31.5	2.40	4.52	5.5		44.90	42.97
KAG7-44	4.12	839		0.29	98	4.5	8.1	1.01	0.51	1.4			
Unknown ge	eologic o	context,	Great S	Sitkin I	sland								
GS725B	2.79	366	21.5	1.23	336	7.6	11.2	2.06	1.72	14.2	0.513051	43.69	42.10

Table A1.5. Compiled Trace Element, Isotope, and Weathering Index data for Aleutian Intrusions, Continued

^aTrace element data from Kay et al. (in revision) except for BW8-55 from Citron (1980); FB53 and FB97 from Kay and Kay (1994); FB44 from Kay et al. (1983); and GS725B from Yogodzinski et al. (2015).

^bNd isotope ratios from Kay et al. (in revision) and references therein except forGS725B from Yogodzinski et al. (2010).

^cChemical Index of Alteration calculated using equation of Nesbitt and Young (1982).

^dMafic Index of Alteration calculated using equation of Babechuk et al. (2014)

APPENDIX A2: SUPPLEMENTARY INFFORMATION FOR CHAPTER 2

Standard Name	Date Run	δ ⁷ Li	Source
Basalt, Hawaii			
BHVO-1	2012 02 22 15:13	4.76	this study
BHVO-1	2012 07 03 13:53	4.81	this study
Average		4.8	
2s		0.1	
BHVO-1		4.0 ~ 5.6	GEOREM database
Basalt, Oregon			
BCR-1	2012 02 22 15:33	3.32	this study
BCR-1	2012 01 12 13:51	2.54	this study
Average		2.9	
2s		1.1	
BCR-1		2 ~ 3	GEOREM database

Table A2.1. Replicate analysis of USGS standards



Figure A2.1. Plot of δ^7 Li versus a. distance from the Aleutian trench (km) and b. depth the Wadati-Benioff Zone (km) in Aleutian lavas. Distance from trench and depth to Wadati-Benioff zone values are from Syracuse and Abers (2006). d⁷Li error bar for Aleutian samples is ±1.0‰.

	Li (ppm)	d ⁷ Li	Nd (ppm)	¹⁴³ Nd/ ¹⁴⁴ Nd							
Depleted Mantle-Se	ediment Melt N	lixing Scena	ario								
Depleted Mantle	0.7^{a}	3.8 ^b	0.713 ^a	0.5131 ^c							
Sediment Melt	83.36 ^d	$2.0^{\rm e}$	4.50^{d}	0.51263^{f}							
Depleted Mantle-Se	ediment Fluid I	Mixing Scen	ario								
Depleted Mantle	0.7^{a}	3.8 ^b	0.713 ^a	0.5131 ^c							
Sediment Fluid	53.66 ^d	15^{g}	13.45 ^d	0.51263^{f}							
Modified Mantle-S	ediment Fluid	Mixing Scer	nario								
Modified Mantle	3.18 ^h	$2.4^{\rm h}$	$0.827^{ m h}$	0.51302^{h}							
Sediment Fluid	53.66 ^d	9.7 ⁱ	13.45 ^d	0.51263 ^f							
^a Salters and Stracke	e (2004)										
^b Average mantle va	alue of Pennsto	n-Dorland e	et al. (2017)								
^c Jicha et al. (2004)											
¹ Calculated using partition coefficients of Johnson and Plank (2000) and assuming 5% fluid or 5% melt in equilibrium with DSDP Hole 183 sediment											

Table A2.2. Values and associated references for mixing scenarios in Figure 2.9

ng 5% fluid or 5% melt in equilibrium with DSDP Hole 183 sediment. assum

^eChan et al. (2006)

^fPlank (2014)

^gSelected as an intermediate composition between the high d⁷Li fluid value of

Tang et al. (20%; 2014) of and the low d⁷Li fluid value of Moriguti and Nakamura (1998).

^hRepresents 3% sediment melt addition to depleted mantle composition from Depleted Mantle-Sediment Melt and Depleted Mantle-Sediment Fluid mixing scenarios.

ⁱMoriguti and Nakamura (1998)



Figure A2.2. Depleted mantle-slab fluid mixing model for δ^7 Li versus ²⁰⁶Pb/²⁰⁴Pb. The + symbol on Depleted Mantle-Sediment Fluid and Modified Mantle-Sediment Fluid Mixing Scenarios indicates 1-3% sediment fluid component. The + symbol on Depleted Mantle-Sediment Melt mixing scenario indicates 1-5% sediment melt component. See Table A2 for values and associated references for the three mixing scenarios. The δ^7 Li error bar for Aleutian samples is ±1.0‰.

	Li (ppm)	d ⁷ Li	Pb (ppm)	²⁰⁶ Pb/ ²⁰⁴ Pb
Depleted Mantle-Se	diment Melt I	Mixing Scena	rio	
Depleted Mantle	0.7^{a}	3.8 ^b	0.0232^{a}	18.3 ^a
Sediment Melt	83.36 ^c	2.0^{d}	16.31 ^c	19.042 ^e
Depleted Mantle-Se	diment Fluid	Mixing Scena	ario	
Depleted Mantle	0.7^{a}	3.8 ^b	0.0232^{a}	18.3 ^a
Sediment Fluid	53.66 ^c	15^{f}	13.69 ^c	19.042 ^e
Modified Mantle-Se	ediment Fluid	Mixing Scen	ario	
Modified Mantle	1.23 ^g	2.8 ^g	0.186 ^g	18.95 ^g
Sediment Fluid	53.66 ^c	9.7 ^h	13.69 ^c	19.042 ^e

Table A2.3. Values and associated references for mixing scenarios in Figure A2

^aSalters and Stracke (2004)

^bAverage mantle value of Pennston-Dorland et al. (2017)

^cCalculated using partition coefficients of Johnson and Plank (2000) and assuming 5% fluid or 5% melt in equilibrium with DSDP Hole 183 sediment.

^dChan et al. (2006)

^ePlank (2014)

^fSelected as an intermediate composition between the high d⁷Li fluid value of

Tang et al. (20‰; 2014) of and the low d^7Li fluid value of Moriguti and Nakamura (1998).

^gRepresents 1% sediment melt addition to depleted mantle composition from Depleted Mantle-Sediment Melt and Depleted Mantle-Sediment Fluid mixing scenarios.

^hMoriguti and Nakamura (1998)

APPENDIX 3: SUPPLEMENTARY DATA AND FIGURES FOR CHAPTER 3

Standard	Ti	Al	Fe	Mg	Mn	Ca	Na	K	Р
BHVO-2									
	15498.73	74347.58	86553.01	40182.38	1362.05	69543.00	16120.88	4483.69	1168.86
	15313.35	74498.94	84324.50	40412.07	1344.53	84530.73	16376.88	4396.85	1153.68
	15125.69	74680.07	82702.95	40780.67	1339.86	84648.93	16287.60	4338.97	1134.72
	15005.85	75032.14	80693.04	40915.29	1327.32	82795.19	16372.24	4287.76	1088.98
	14912.39	76057.86	78560.61	41504.50	1312.16	82293.60	16658.72	4238.23	1098.01
	14842.23	77236.27	77151.95	41710.73	1310.93	82724.37	16629.07	4224.75	1078.84
	14616.57	76177.81	75790.48	41421.82	1302.06	81911.61	16658.84	4151.71	1056.47
	14608.11	75148.45	74564.63	41126.29	1293.32	80738.51	16580.24	4128.81	1075.14
	14576.38	76370.77	73407.42	41431.30	1290.09	81156.69	16602.66	4118.96	1059.02
Average	14944.37	75505.54	79305.40	41053.90	1320.26	81149.18	16476.35	4263.30	1101.52
Uncertainty (2 SD)	650.96	1985.97	9110.32	1044.71	49.44	9100.46	386.88	251.21	82.38
Accuracy	-8.76	5.65	-7.89	-5.36	2.35	-0.34	0.03	-1.20	-6.56

Table A3.1a. Replicate Analysis of BHVO-2 Major Elements in Parts Per Million.

Standard	Ti	Al	Fe	Mg	Mn	Ca	Na	K	Р
SBC-1									
	4876.45	118072.58	69551.10	15698.25	1207.98	26190.75	-	29069.88	1656.90
	4779.88	119146.16	67526.11	15370.82	1196.50	21506.70	-	27746.61	1614.64
	4742.38	118109.91	65873.51	15160.97	1186.50	21110.49	-	26961.02	1540.87
	4759.61	117179.00	64905.41	15124.95	1184.25	21225.41	-	26476.32	1539.56
	4689.09	121332.99	62713.49	15559.82	1167.39	20922.97	-	25711.90	1504.98
	4675.01	119869.18	61854.17	15318.63	1167.28	20770.95	-	25157.81	1504.92
	4596.97	119745.13	60867.32	15301.37	1158.76	20510.08	-	24371.54	1484.11
	4629.50	119927.44	60460.56	15182.13	1157.40	21255.64	-	24186.50	1487.67
	4602.62	117453.24	59494.00	15011.36	1150.03	21922.20	-	23740.77	1512.76
Average	4705.72	118981.74	63693.96	15303.15	1175.12	21712.80	-	25935.82	1538.49
Uncertainty (2 SD)	184.91	2737.97	6915.21	435.07	39.26	3457.25	-	3565.47	118.91
Accuracy	-8.27	7.02	-6.29	-1.90	1.13	3.05	-	-9.40	-4.74

Table A3.1b. Replicate Analysis of SBC-1 Major Elements in Parts Per Million

Standard	Li	V	Cr	Co	Ni	Cu	Rb	Sr	Y	Zr	Nb	Ba	Ta	Pb
BHVO-2														
	4.06	327.42	295.95	45.68	125.38	-	8.88	-	23.12	164.76	16.00	128.23	-	-
	4.15	327.06	293.72	45.72	125.68	-	8.97	-	22.90	165.50	15.99	128.22	-	-
	4.32	323.79	292.29	45.26	125.34	-	9.34	-	23.03	166.68	16.18	129.06	-	-
	4.45	322.76	290.77	45.10	124.73	-	9.35	-	23.08	167.33	16.35	127.30	-	-
	4.48	320.76	288.34	44.87	123.86	-	9.48	-	23.70	170.36	16.41	129.10	-	-
	4.60	318.31	287.37	44.66	123.39	-	9.61	-	24.00	174.48	16.91	129.08	-	-
	4.70	317.19	286.77	44.56	122.89	-	9.82	-	23.66	171.74	16.71	127.26	-	-
	4.83	316.21	285.19	44.26	122.24	-	9.87	-	23.54	170.77	16.44	128.95	-	-
	4.95	316.24	284.95	44.30	122.89	-	10.00	-	23.74	172.94	16.96	126.11	-	-
Average	4.51	321.08	289.48	44.93	124.04	-	9.48	-	23.42	169.40	16.44	128.15	-	-
Uncertainty (2 SD)	0.60	8.83	7.79	1.09	2.55	-	0.78	-	0.78	6.89	0.72	2.11	-	-
Accuracy	0.12	1.29	3.39	-0.15	4.24	-	-3.26	-	-9.61	-1.05	-8.68	-1.43	-	-

Table A3.2a. Replicate Analysis of BHVO-2 Trace Elements in Parts Per Million

Table A3.2b. Replicate Analysis of SBC-1 Trace Elements in Parts Per Million.

Standard	Li	V	Cr	Co	Ni	Cu	Rb	Sr	Y	Zr	Nb	Ba	Ta	Pb
SBC-1														
	171.35	230.82	113.86	23.74	91.42	34.17	156.26	194.99	31.47	114.26	14.33	802.57	0.99	37.09
	171.87	229.16	113.94	23.78	92.14	33.57	157.64	189.10	31.66	115.85	14.55	828.00	1.00	37.66
	168.96	228.48	113.10	23.51	91.62	33.46	154.71	186.20	31.75	116.61	14.60	823.19	1.01	38.24
	171.54	227.84	113.38	23.54	91.43	33.44	155.14	185.88	32.12	117.79	15.12	825.31	1.02	38.07
	172.35	225.12	111.84	23.26	90.30	32.96	156.40	189.88	32.42	119.56	15.22	819.78	1.02	38.13
	172.29	226.09	111.82	23.31	90.16	33.04	156.30	188.17	32.46	119.90	15.24	822.89	1.05	38.83
	173.51	224.64	110.81	23.32	90.20	33.01	156.18	185.94	32.66	119.45	15.30	828.25	1.05	39.23
	177.50	223.87	110.92	23.30	89.83	32.85	156.28	185.92	32.77	120.43	15.66	826.55	1.05	38.63
	176.37	222.35	110.95	23.11	89.56	33.02	155.76	183.70	32.57	120.39	15.26	823.07	1.06	38.72
Average	172.86	226.49	112.29	23.43	90.74	33.28	156.07	187.76	32.21	118.25	15.03	822.18	1.03	38.29
Uncertainty (2 SD)	5.25	5.53	2.58	0.46	1.84	0.84	1.66	6.63	0.96	4.46	0.87	15.69	0.05	1.31
Accuracy	6.05	2.95	3.02	3.21	9.59	7.35	6.17	5.48	-11.76	-11.76	-1.75	4.34	-6.47	9.39

Standard Ce Eu Tb Dy Ho Er La Pr Nd Sm Gd Tm Yb Lu BHVO-2 13.85 35.75 4.78 21.42 5.84 1.84 5.46 0.84 5.49 0.98 2.28 0.34 1.85 0.25 13.97 35.04 4.82 21.82 5.92 1.87 5.59 0.87 5.57 0.97 2.32 0.34 1.85 0.25 14.45 35.95 4.98 22.58 5.99 1.95 5.77 0.89 5.55 0.99 2.41 0.33 1.90 0.26 14.57 35.77 5.04 22.98 6.01 1.97 5.79 0.91 5.61 0.98 2.43 0.35 1.93 0.26 14.76 35.35 5.09 23.09 6.11 1.99 5.88 0.90 5.63 1.00 2.44 0.34 1.96 0.26 14.98 35.15 5.17 23.40 6.33 2.02 5.95 0.92 5.74 1.01 2.47 0.34 1.97 0.27 5.36 24.39 6.32 2.09 6.20 0.96 5.71 1.00 2.63 15.46 36.55 0.34 2.02 0.28 15.52 35.83 5.39 24.55 6.46 2.10 6.28 0.97 5.63 1.00 2.62 0.34 1.99 0.29 15.56 35.61 5.40 24.62 6.18 2.11 6.30 0.98 5.64 1.02 2.60 0.34 2.01 0.29 14.79 35.67 5.11 23.21 6.13 1.99 5.91 0.92 5.62 0.99 2.47 0.34 1.94 0.27 Average Uncertainty 1.29 0.91 0.47 2.33 0.42 0.20 0.59 0.09 0.16 0.03 0.26 0.01 0.13 0.03 (2 SD) -1.40 -4.89 -3.68 -4.38 1.76 -2.44 -4.74 1.79 6.44 2.53 -1.73 1.48 -2.53 -0.53 Accuracy

Table A3.3a. Replicate Analysis of BHVO-2 Rare Earth Elements in Parts Per Million

Table A3.3b. Replicate Analysis of SBC-1 Rare Earth Elements in Parts Per Million.

Standard	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SBC-1														
	52.60	106.89	12.12	45.92	9.66	1.99	8.29	1.17	7.28	1.31	3.48	0.56	3.36	0.48
	52.08	107.41	12.34	46.71	9.83	2.02	8.40	1.18	7.28	1.32	3.51	0.54	3.36	0.48
	51.29	104.11	12.29	46.34	10.11	2.01	8.31	1.18	7.52	1.35	3.51	0.55	3.39	0.48
	51.19	106.48	12.61	47.64	10.32	2.05	8.51	1.21	7.50	1.35	3.58	0.56	3.39	0.49
	52.48	107.86	12.93	48.91	10.27	2.12	8.84	1.24	7.41	1.34	3.68	0.56	3.51	0.51
	51.97	106.70	13.16	49.87	10.48	2.13	8.98	1.27	7.65	1.36	3.78	0.56	3.52	0.52
	51.62	107.05	13.22	49.97	10.59	2.17	8.95	1.29	7.56	1.38	3.77	0.58	3.57	0.52
	52.35	107.29	13.50	51.23	10.53	2.23	9.23	1.31	7.42	1.37	3.91	0.56	3.55	0.54
	52.27	107.35	13.64	51.51	10.90	2.25	9.27	1.33	7.39	1.35	3.95	0.56	3.57	0.54
Average	51.98	106.79	12.87	48.68	10.30	2.11	8.75	1.24	7.45	1.35	3.68	0.56	3.47	0.51
Uncertainty (2 SD)	1.02	2.17	1.11	4.23	0.77	0.19	0.77	0.12	0.25	0.04	0.36	0.02	0.19	0.05
Accuracy	-0.98	-1.12	2.12	-1.06	7.27	6.45	2.96	3.58	4.87	-3.75	-3.04	-0.42	-4.71	-6.04



Figure A3.1. τ_j versus a. percent anothite and b. percent forsterite for Cerro Colorado samples. See text for details.



Figure A3.2. τ_j versus percent forsterite for San Joaquin 2 samples. See text for details.



Figure A3.3. Percent hematite + goethite versus a. Na and K and b. Ca, Sr, and Mn for San Joaquin 2 samples. See text for details.



Figure A3.4. τ_j versus percent kaolin minerals for San Joaquin 2 samples. See text for details.



Figure A3.5. τ_j versus percent gibbsite for San Joaquin 1. See text for details.



Figure A3.6. τ_j versus a. percent gibbsite and b. percent kaolin minerals for San Joaquin 1 samples. Symbols are the same in a and b. See text for details.



Figure A3.7. τ_j versus percent Fe oxides and oxyhydroxides for San Joaquin 1 samples. See text for details.



Figure A3.8. Percent Fe oxides and oxyhydroxides versus a. Sr, Na, and Mg and b. Ba for Socavòn samples. See text for details.



Figure A3.9. Percent Fe oxides and oxyhydroxides versus K and Rb for Socavon samples. See text for details.



Figure A3.10. Percent forsterite versus a. V, Cr, and Co and b. Ni, P, and Mn for Cerro Colorado samples. See text for details.



Figure A3.11. τ_j versus a. percent forsterite and b. percent augite for San Joaquin 2 samples. See text for details.



Figure A3.12. τ_j versus percent Fe oxides and oxyhydroxides for San Joaquin 2 samples. See text for details.



Figure A3.13. Percent gibbsite versus a. P, Cu, and Mn and b. Co and Ni for San Joaquin 1 samples. See text for details.



Figure A3.14. τ_j versus a. percent gibbsite and b. percent kaolin minerals for San Joaquin 1 samples. Symbol is the same in a and b. See text for details.



Figure A3.15. τ_j versus a. percent kaolin minerals and b. percent gibbsite for San Joaquin 1 samples. See text for details.



Figure A3.16. Percent Fe oxides and oxyhydroxides versus a. V Mn, and Pb and b Co and Cu. Socavon samples. See text for details.



Figure A3.17. τ_j versus percent kaolin minerals for Socavon samples. See text for details.



Figure A3.18. τ_j versus percent augite for Cerro Colorado samples. See text for details.



Figure A3.19. τ_j versus a. percent augite + Anorthite and b. % anorthite for San Joaquin 2 samples. See text for details.



Figure A3.20. τ_j versus a. percent gibbsite and b. percent kaolin minerals for San Joaquin 1 samples. See text for details.



Figure A3.21. τ_j versus a. percent Fe oxides and oxyhydroxides and b. percent hematite minerals for Socavon samples. See text for details.


Figure A3.22. Percent kaolin minerals versus τ_{Zr} and τ_{Y} . See text for details.



Figure A3.23. τ_j versus percent a. kaolin minerals for Chadwick et al. (2003) profile E, and b. sesquioxides for Chadwick et al. (2003) profile B. See text for details.



Figure A3.24. τ_{Na} versus a. percent hematite + goethite for San Joaquin 2 and Nelson et al. (2013), and b. sesquioxides for Chadwick et al. (2003) profiles I and J. See text for details.



Figure A3.25. τ_K versus percent hematite + goethite for Nelson et al. (2013). See text for details.



Figure A3.26. τ_{Mg} versus a. sesquioxides for Chadwick et al. (2003) profile J, and b. kaolin minerals for Nelson et al. (2013). See text for details.



Figure A3.27. τ_j versus percent kaolin minerals for Nelson et al. (2013). See text for details.



Figure A3.28. τ_{AI} versus a. sesquioxides for Chadwick et al. (2003) profile I, and b. kaolin minerals for Nelson et al. (2013) and Chadwick et al. (2003) profile J. See text for details.



Figure A3.29. τ_{Ca} versus percent mineral for kaolin minerals in site M, and sesquioxides in site L from Chadwick et al. (2003). See text for details.



Figure A3.30. τ_{Mg} versus a. gibbsite + kaolin minerals for the Columbia and Cowlitz profiles from Liu et al. (2013), and b. sesquioxides for Chadwick et al. (2003) profile L. See text for details.



Figure A3.31. τ_{Mg} versus a. gibbsite + kaolin minerals for the Columbia and Cowlitz profiles of Liu et al. (2013), and b. hematite + goethite for profile 1 of Sowards et al. (2018). See text for details.



Figure A3.32. τ_K versus percent mineral for gibbsite + kaolin minerals in the Cowlitz core of Liu et al. (2013); kaolin minerals in Chadwick et al. (2003) site M; and goethite + hematite in profile 1 of Sowards et al. (2013). See text for details.



Figure A3.33. τ_P versus gibbsite + kaolin minerals for the Columbia and Cowlitz profiles of Liu et al. (2013). See text for details.



Figure A3.34. τ_{Mn} versus kaolin minerals for profile 2 of Sowards et al. (2018). See text for details.



Chadwick et al. (2003) Profile L (Sesquioxides) Sowards et al. (2018) Profile 1 (Gibbsite)

Figure A3.35. τ_{A1} versus a. gibbsite for Sowards et al. (2018) profile 1 and sesquioxides for Chadwick et al. (2003) profile L; and b. gibbsite + kaolin minerals for the Columbia and Cowlitz profiles of Liu et al. (2013). See text for details.



Figure A3.36. τ_{Ti} versus gibbsite for the Columbia profile and gibbsite + kaolin minerals for the Cowlitz profile of Liu et al. (2013). See text for details.



Figure A3.37. τ_j versus percent a. hematite + goethite, and b. kaolin minerals from Nelson et al. (2013). See text for details.



Figure A3.38. Chondrite-normalized REE values for San Cristobal rocks and Cerro Colorado samples reveal that Cerro Colorado samples are LREE-enriched, not LREE-depleted like the Puerto Chino rock. Thus, an average composition of the rocks from the Socavòn, San Joaquin 2, San Joaquin 1, and El Junco sites more accurately approximates a Cerro Colorado parent composition than the Puerto Chino rock. See text for additional details.

APPENDIX 4: SUPPLEMENTARY FIGURES FOR CHAPTER 4



Figure A4.1. Correlation between depth and (La/Lu)_{Parent} for San Joaquin 1 samples. See text for details.



Figure A4.2. (La/Lu)_{Parent} versus a. kaolin minerals and b. gibbsite for San Joaquin 1 samples. See text for details.



Figure A4.3. Eu anomaly versus τ_{Al} for San Joaquin 1 and Socavòn samples. Green trendline represents all San Joaquin 1 samples, while blue trendline represents San Joaquin 1 samples except for 100 cm and 120 cm, which have anomalously low Eu anomalies compared to the surrounding samples. See text for details.



Figure A4.4. Ce anomaly versus percent Fe oxides and oxyhydroxides in Socavon samples. See text for details.