Strong climate and tectonic control on plagioclase weathering in granitic terrain

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ABSTRACT

Investigations to understand linkages among climate, erosion and weathering are central to quantifying landscape evolution. We approach these linkages through synthesis of regolith data for granitic terrain compiled with respect to climate, geochemistry, and denudation rates for low sloping upland profiles. Focusing on Na as a proxy for plagioclase weathering, we quantified regolith Na depletion, Na mass loss, and the relative partitioning of denudation to physical and chemical contributions. The depth and magnitude of Na depletion increased continuously with increasing water availability, except for locations with mean annual temperature <5 °C that exhibited little Na depletion, and locations with physical erosion rates <20 g m⁻² yr⁻¹ that exhibited deep and complete Na depletion. Surface Na depletion also tended to decrease with increasing physical erosion. Depth-integrated Na mass loss and Na depletion depth were both three orders of magnitude greater in the fully depleted, low erosion rate sites relative to other locations. These locations exhibited strong erosion-limited depletion of Na chemical weathering rates based on correlation of Na chemical weathering rate to total Na denudation. Sodium weathering rates in cool locations with positive annual water balance were strongly correlated to total Na denudation and precipitation, and exhibited an average apparent activation energy (Ea) of 69 kJ mol⁻¹ Na. The remaining water-limited locations exhibited kinetic limitation of Na weathering rates with an Ea of 136 kJ mol⁻¹ Na, roughly equivalent to the sum of laboratory measures of Ea and dissolution reaction enthalpy for albite. Water availability is suggested as the dominant factor limiting rate kinetics in the water-limited systems. Together, these data demonstrate marked transitions and nonlinearity in how climate and tectonics correlate to plagioclase chemical weathering and Na mass loss.

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1. Introduction

What controls the thickness and chemistry of the Earth’s regolith? Answering this question is fundamental to understanding landscape evolution, soil-forming processes, and the feedback between mineral weathering, the global cycling of chemical elements, and atmospheric carbon dioxide (Berner et al., 1983; Raymo and Ruddiman, 1992). On upland landscapes, the chemistry and thickness of regolith, defined here to include soil and saprolite layers down to the depth of unweathered bedrock, are thought to be controlled by parent material mineralogy, precipitation, temperature, physical erosion, biota, and dust input (Dokuchaev, 1967; Jenny, 1941). The lack of models that can predict the thickness and chemistry of regolith as a function of these variables is due to difficulties in deciphering the relative contribution of each variable, as well as observed thresholds in soil development (Chadwick and Chorover, 2001), landscape evolution (Phillips, 2006), and mineral weathering (Kump et al., 2000). Climate is considered a central control on regolith formation, manifest as water availability and temperature (White, 1995). Water causes silicate hydrolysis and transports soluble weathering products away from reaction sites, whereas temperature controls weathering rates and mineral solubility (Lasaga et al., 1994). Temperature also moderates water availability through its control on the partitioning of precipitation to evapotranspiration and base-flow (L’vovich, 1979). Variation in climate is coupled with concomitant variation in biota and biotic influences on chemical weathering via transfer of CO₂ and reduced carbon compounds into the regolith. However, the direct role of biota can be very difficult to separate from climate because of their strong interaction and covariance (Amundson et al., 2007). Biogeochemical studies demonstrate strong control of water and temperature on both elemental loss and chemical weathering rates across laboratory to watershed space and time-scales (Kump et al., 2000; Velbel, 1993; White et al., 1999). Similarly, soil climosequence studies demonstrate a strong correlation of climate to soil chemistry and mineral
transformation in landscapes of low physical erosion (Chadwick et al., 2003; Dahlgren et al., 1997; Rasmussen et al., 2007; Williams et al., 2010). However, climosequence studies are generally designed to minimize the effects of physical erosion, and focus largely on the imprint of climate on soil properties as recorded by within-pedon mineral transformation and mass redistribution. In comparison, recent empirical geomorphic work at watershed and hillslope scales demonstrates that for moderately eroding landscapes, physical erosion exerts primary control on chemical weathering rates, with climate as a second order constraint (Hren et al., 2007; Jacobson et al., 2003; Riebe et al., 2004; West et al., 2005). This contrasts substantial watershed biogeochemistry work noting strong temperature correlation to weathering rates (Dorn and Brady, 1995; Turner et al., 2010; White and Blum, 1995), and recent geomorphic work suggesting strong climate relation to soil and saprolite chemical weathering (Dixon et al., 2009b). The complete nature of the climate-erosion interaction and its control on the biogeochemical processes of chemical mass loss, weathering rate, and regolith formation thus remains poorly defined.

At the hillslope scale, controls on the physical transport of regolith material have been explored using the concepts of transport- and weathering-limitation (Carson and Kirkby, 1972; Gilbert, 1877), with later work linking these regimes to large river basin denudation and solute chemistry (Stallard and Edmond, 1983). Similar notions have recently been used to describe and model the relation of physical erosion and mineral supply to chemical weathering rates, expressed simply as (Ferrier and Kirchner, 2008; Gabet and Mudd, 2009; Millot et al., 2002; West et al., 2005): \( W = E^\lambda \), where \( W \) is chemical weathering rate, \( E \) is the physical erosion and assumed equivalent to the rate of mineral supply into the regolith under steady-state conditions, and \( \lambda \) is a dimensionless constant. Values of \( \lambda \approx 1 \) are attributed to regimes where physical erosion limits chemical weathering, whereas \( \lambda < 1 \) indicates regimes limited at least partially by chemical weathering kinetics. Others have suggested that relating chemical weathering to total landscape lowering or denudation \( (D) \), where \( D = E + W \) presents a better framework for indentifying physical constraints on chemical weathering rates (Riebe et al., 2004). This may be particularly important for landscapes that experience substantial chemical weathering at depth in saprolite layers that are not physically transported (Dixon et al., 2009a).

In these systems, the total chemical weathering rate \( (W_{\text{total}}) \) is the sum of weathering occurring in upper soil layers susceptible to physical transport \( (W_{\text{soil}}) \) and isolomuvetic weathering occurring in saprolite \( (W_{\text{sap}}) \), where: \( W_{\text{total}} = W_{\text{soil}} + W_{\text{sap}} \). Such that total landscape lowering or total denudation is equivalent to \( (D) \) and is used extensively in soil science \((\text{Soil Survey Staff, 1999})\). In this study, we focused on linking regolith geochemical profiles and chemical weathering rates to climate and erosion data. Regolith is defined here to include soil and saprolite layers down to the depth of unweathered bedrock defined as the “depth of refusal”, the contact where regolith can no longer be excavated by hand, hydraulic core, or drill \((\text{Soil Survey Staff, 1999})\). The compiled data were limited to regolith developed on granitic rocks in locations little disturbed by human activities as reported for idealized 1-dimensional weathering profiles, i.e., upland, ridge-top positions with minimal to no colluvial material \((\text{Taylor and Eggleton, 2001})\) \((\text{Table A1})\). Ridge-top locations represent the simplest possible landscape positions with 1-dimensional vertical processes dominating soil production and chemical weathering \((\text{Brantley and White, 2009})\). Limiting data to one landscape position eliminates the effects of slope steepness, downslope transport, and colluvial layer thickness on regolith development \( (\text{Yoo et al., 2007}) \). Data were excluded only for cases where there were clear lithologic discontinuities in the regolith profile such as glacial till over bedrock, surface slope was greater than 7.5°, or where rock geochemistry was poorly constrained. The slope angle of 7.5° was chosen based on field and laboratory data indicating that slopes of less than 7.5° exhibit lower runoff coefficients and higher infiltration rates relative to steeper landscape positions that indicate water is more likely to infiltrate vertically and hence promote 1-dimensional regolith weathering \((\text{Chaplot and Le Bissonnais, 2000; Fox et al., 1997})\).

For the data included here, the sites were concentrated in the mid-to low-latitudes \((18 \text{ to } 40^\circ \text{ N and S})\) with an average mean annual precipitation \((\text{MAP})\) that ranged from 370 to 4200 mm yr\(^{-1}\) and average mean annual air temperature \((\text{MAT})\) that ranged from 3.9 to 30.0°C \((\text{Table A1})\). Water availability was quantified using a simple dimensionless “humidity index”, equivalent to mean annual precipitation divided by mean annual potential evapotranspiration \((\text{PET})\): \( \text{HI} = \text{MAP}/\text{PET} \), where \( \text{HI} \) is humidity index and both MAP and PET are in units of length per unit time. The humidity index, a standard approximation of annual water balance, is used extensively in soil science \((\text{Buol et al., 2003})\) and hydrology \((\text{Brunsøt, 2005})\). Humidity index values greater than one indicate positive annual water balance, whereas values less than one indicate negative annual water balance. Following hydrologic convention, we use the terms “energy-limited” when \( \text{HI} > 1 \) and precipitation exceeds the energy available for evapotranspiration, and “water-limited” when \( \text{HI} < 1 \) and evapotranspiration is limited by the amount of precipitation \((\text{Budyko, 1974})\). We recognize that an annual humidity index does not capture short-term variation of soil–water dynamics, water residence time or solute composition that are important mechanistic controls on mineral weathering over daily to annual time-scales \((\text{Maher, 2010})\). However, an annual humidity index provides a meaningful empirical proxy for decadal scale water availability that can provide insight as to the role of climate in regolith formation \((\text{Jenny, 1941})\).

The humidity index was calculated using site-specific precipitation data and potential evapotranspiration calculated from mean monthly temperature and latitude \((\text{Black, 1996; Thornthwaite, 1948})\). The Thornthwaite method requires only monthly mean temperature and
latitudinal, and despite its simplicity has been acknowledged as providing meaningful PET estimates when limited climate data are available (Black, 2007). We recognize that methods such as Penman–Monteith provide a more accurate physical approximation of evapotranspirative processes (Brutsaert, 2005). However, Penman–Monteith requires substantial climate and site-specific data that were not readily available for the majority of locations. The majority of locations included here only report MAP and MAT, but the Thornthwaite method requires monthly temperature data. We therefore accessed the global temperature dataset of New et al. (1999) that provides mean monthly temperature estimates averaged over 1961–1995. Potential evapotranspiration was calculated monthly and summed to provide an annual estimate of PET.

2.2. Chemical depletion and mass flux

Chemical depletion was analyzed by focusing on net loss of Na as a proxy for plagioclase weathering. Dissolution of plagioclase is often the first reaction to create significant porosity during weathering and thus of central importance in the conversion of granitic rock to regolith (Brantley and White, 2009). Furthermore, Na is found predominantly in plagioclase in granites and is not significantly incorporated into clays in most regolith. Net Na loss and gain was quantified using a dimensionless mass transfer coefficient (\(\tau_{Na}\)) (Anderson et al., 2002):

\[
\tau_{Na} = \frac{C_{Na,w}Zr,p}{C_{Na,p}Zr,w} - 1.
\]

Here, \(C\) (M\(^{-1}\)) is the weight percent concentration of an element, subindex \(Na\) refers to the mobile element sodium, subindex \(Zr\) refers to the immobile reference element Zr, subindex \(w\) refers to weathered regolith, and subindex \(p\) refers to parent material. Positive \(\tau_{Na}\) values indicate net gain and negative values net loss of Na from the regolith relative to the parent material.

A primary assumption of this type of analysis is the immobility of the reference element, in this case Zr. Zirconium mobility has been reported in the literature, particularly for mafic volcanic terrain where Zr may be present in Fe and Ti-oxides, micas, pyroxenes, and amphiboles that are susceptible to dissolution and transport (Kurtz et al., 2000). In granitic terrain, Zr is typically located in unweatherable and immobile zircon (Neaman et al., 2006). However, zirconium mobility has been documented for granitic terrain in wet tropical environments (Viers et al., 1997) and this mobility may be especially important in the presence of high organic ligand concentrations (Viers et al., 2000). Here, data for only one wet tropical location were included in this study, a regolith profile from the Luquillo Experimental Forest in Puerto Rico (Table A1). In that system, very little dissolved organic carbon is present in porewaters at depths where plagioclase weathering occurs, perhaps explaining why both Ti and Zr were essentially immobile during regolith weathering (White et al., 1998). Furthermore, Hodson (2002) reported that Zr was the least mobile element in leaching experiments of granitic A and B soil horizons, and that relative to Na, Zr mobility would result in at most a ~1% relative underestimate of Na loss. This potential 1% underestimate in Na loss due to putative Zr mobility is included in the error propagation (see Electronic Supplement Section A.2).

The Na mass transfer coefficient was used to calculate a time-integrated regolith mass flux of Na (\(M_{Na,flux}\); M\(^{-2}\) L\(^{-1}\)) summed over the entire regolith depth (\(h = \) depth of refusal; L). This value represents the total loss of Na from the regolith to chemical weathering with respect to the reference immobile element, integrated over the time scale of regolith mean residence time (Chadwick et al., 1990; White et al., 2001):

\[
M_{Na,flux} = \sum_{i=1}^{n} \frac{C_{Na,p}Zr,p}{100} \rho_{Na} \tau_{Na}(i) \cdot z(i).
\]

where \(\rho_{Na}\) (M\(^{-2}\) L\(^{-3}\)) is parent material density (\(\approx 2.65\) g cm\(^{-3}\)) and \(z\) (L) is depth of horizon \(i\).

2.3. Denudation rates

A subset of sites reported cosmogenic radionuclide-derived denudation rates (\(D_{CRN}\)) (Table A1). This denudation rate is defined as the rate of loss of material from chemical and physical processes over the cosmic ray penetration depth (\(\approx 1–2\) m). For a steady-state regolith depth, \(D_{CRN} = E + W_{CRN}\), where \(E\) and \(W_{CRN}\) are rates of physical erosion and the average chemical weathering rate over the entire cosmogenic penetration zone, respectively, scaled to the land area (M\(^{-1}\) L\(^{-2}\) T\(^{-1}\)) (Riebe et al., 2001, 2003). To include landscapes that experience chemical weathering in saprolite and layers beyond the cosmic ray penetration depth, we follow Dixon et al. (2009a) and expand this equation to solve for total regolith denudation or landscape lowering as \(D_{total} = D_{CRN} + W_{sap}\), where \(W_{sap}\) is chemical weathering rate for Na below the cosmic ray penetration depth, assumed to be saprolite weathering isovolumetrically (Ollier and Pain, 1996). Total regolith chemical weathering rate \(W_{total}\) is thus the sum of \(W_{CRN}\) and \(W_{sap}\) and total denudation the sum of physical erosion and total chemical weathering:

\[
D_{total} = E + W_{total}.
\]

Isovolumetric saprolite weathering is assumed in part based on the substantial body of research documenting this phenomenon in granitic terrain (Gardner et al., 1978; Grant, 1963; Millor, 1970; Price and Velbel, 2003). For about one quarter of the sites included in this synthesis, the volumetric strain \(\varepsilon\) was calculated for each horizon of the regolith profile using: \(\varepsilon = \rho_{p}Zr,p/\rho_{Na}Zr,w - 1\), where values that approach zero indicate no volume change (Brimhall and Dietrich, 1987). All of the locations with strain data indicate values near zero in saprolite layers, verifying the isovolumetric weathering assumption (Oh and Richter, 2005; Schroeder et al., 2002; White et al., 1998, 2001). Also, as noted previously, plagioclase weathering is typically the primary chemical weathering reaction in granitic saprolite, with the most substantial plagioclase loss in the regolith profile often occurring at the rock to saprolite transition (e.g., White et al., 2001). Plagioclase loss generally occurs via pseudomorphic replacement by kaolin (Buol and Weed, 1991), resulting in at most a 10% decrease in volume (Taylor and Eggleton, 2001: p. 206). Weathering of mica and the potential associated volumetric expansion (Graham et al., 2010) appears to be minimal in the noted studies even where this reaction may have driven fracturing, and indeed, muscovite concentrations changed little from rock to soil surface in the locations summarized by White et al. (2001), and biotite persists throughout the regolith profile even under extreme weathering conditions of the wet, tropical Luquillo profile (Buss et al., 2005, 2008). Based on these data we assume that an isovolumetric saprolite weathering is valid across all locations.

We assume that physical erosion occurs due to loss of material from the soil surface and that regolith depth is constant in time. We then define the weathering advance rate as the conversion of bedrock to saprolite in units of M\(^{-2}\) T\(^{-1}\) (\(D_{sap}\)). This term can be related to the total denudation determined from cosmogenic nuclides, \(D_{CRN}\), through conservation of mass for a chemically immobile element such as Zr (Dixon et al., 2009a):

\[
D_{sap}Zr,p = D_{CRN}Zr,sap = EC_{zr,CRN}Zr,CRN
\]

where \(C_{zr,CRN}\) is saprolite Zr concentration at the soil-saprolite interface or at the bottom of the cosmogenic isotope penetration depth, and \(C_{zr,CRN}\) is the depth weighted average Zr concentration over the depth of cosmogenic isotope penetration and layers susceptible to physical transport. Physical erosion may thus be calculated as:

\[
E = D_{CRN}Zr,sap / C_{zr,CRN}
\]

and the total denudation rate expressed as a function of the weathering advance rate:

\[
D_{total} = D_{sap} = D_{CRN} \left( \frac{C_{zr,sap}}{C_{zr,rock}} \right)
\]
The total denudation rates for sites included here ranged from 13 to 191 g m\(^{-2}\) yr\(^{-1}\) with a mean of 101 ± 11 g m\(^{-2}\) yr\(^{-1}\) (± standard error), equivalent to a range of 0.005 to 0.072 mm yr\(^{-1}\) and mean of 0.038 ± 0.004 mm yr\(^{-1}\) (Table A1). These rates are at or below the globally averaged estimate of total land surface denudation of 0.062 mm yr\(^{-1}\) (Wilkinson and McElroy, 2007), and far below denudation rates calculated for areas of rapid tectonic uplift that can be on the order of to 10 to 20 mm yr\(^{-1}\) (Burbank, 2002; Montgomery and Brandon, 2002). The data synthesized here thus represent landscapes with slow to moderate denudation rates.

Partitioning of total denudation to chemical weathering was accomplished using the “chemical depletion fraction” (CDF), equivalent to the ratio of \(W_{\text{CRN}}\) to \(D_{\text{CRN}}\), whereby (Riebe et al., 2004): \(W_{\text{CRN}} = D_{\text{CRN}} \cdot \text{CDF}\). In this equation, CDF equals \(\tau\) averaged over the regolith thickness penetrated by cosmogenic rays (\(\sim \tau_{\text{CRN}}\)). Total Na weathering rates were thus estimated using \(\tau_{\text{Na,CRN}}\) values and \(D_{\text{total}}\) from Eq. (3) with total Na weathering rate \(W_{\text{Na,total}}\) equivalent to:

\[
W_{\text{Na, total}} = D_{\text{total}} (−\tau_{\text{Na,CRN}}).
\]

### 2.4. Modeling of weathering rate controls

The relationship of total Na weathering rate to precipitation, temperature, and total Na denudation rate was quantified using a simple linear empiricism (Riebe et al., 2004): \(W_{\text{Na,total}} = \alpha(D_{\text{Na,total}})^\gamma \exp(−\frac{Ea}{R \cdot \text{MAT}})\), where the first term is the total Na denudation rate \(D_{\text{Na,total}}\) (mol Na m\(^{-2}\) yr\(^{-1}\)) defined here as total denudation \(D_{\text{total}}\) g m\(^{-2}\) yr\(^{-1}\) times the bedrock Na molar concentration \(C_{\text{Na,bed}}\) (mol Na g\(^{-1}\) rock), and \(\alpha\) and \(\gamma\) are empirical coefficients; the second term is an Arrhenius function describing the influence of temperature in which \(Ea\) is the apparent activation energy (J mol\(^{-1}\)), \(R\) is the universal gas constant, and \(\text{MAT}\) (°K); and the third term is mean annual precipitation, with \(\gamma\) an empirical coefficient. Correlation analysis of the independent variables indicated no significant correlation. The function was solved for \(\tau\), \(\gamma\), and \(Ea\) using the linearized form of this equation and stepwise multiple linear regression:

\[
\ln(W_{\text{Na,total}}) = \ln(\alpha) + \gamma \ln(D_{\text{Na,total}} / D_{\text{Na,total,REF}}) + \frac{Ea}{R(1 / \text{MAT}_{\text{REF}} − 1 / \text{MAT})} + \gamma \ln(M\text{AT} / \text{MAT}_{\text{REF}}),
\]

where \(D_{\text{Na,total,REF}}\) is the average mineral supply rate for the dataset (0.090 mol Na m\(^{-2}\) yr\(^{-1}\)), \(\text{MAT}_{\text{REF}}\) is the average mean annual temperature for the dataset (14.7 °C), and \(\text{MAT}_{\text{REF}}\) is the average mean annual precipitation for the dataset (912 mm yr\(^{-1}\)).

### 3. Results and discussion

#### 3.1. Regolith depletion profiles

Depth profiles of \(\tau_{\text{Na}}\) define chemical depletion profiles that vary from partially depleted where \(0 > \tau_{\text{Na}} > −1\) at the surface, to completely depleted profiles where \(\tau_{\text{Na}} ≈ −1\) at the surface (Brantley and White, 2009). Both partially and fully depleted profiles were observed, with a distinct distribution of depletion profile depth and form according to both physical erosion rate and climate (Figure 1). The data were separated into three groups based on extent of profile depletion and climate: (i) those with complete Na depletion of the upper regolith profile; (ii) those with partial Na depletion and HI > 1; and (iii) those with partial depletion and HI < 1 (Figure 1a-c, respectively).

The deepest and most fully depleted Na profiles occurred in landscapes with physical erosion rates less than 20 g m\(^{-2}\) yr\(^{-1}\), equivalent to less than 0.008 mm yr\(^{-1}\) (Table 1). All of these profiles exhibited near complete Na loss to depths of up to 6 m below the soil surface, with most sites exhibiting a relatively abrupt decrease in Na depletion at the saprolite-rock interface (Figure 1a). The lack of Na in soil and upper saprolite indicates that the active Na weathering front occurs at the saprolite-rock interface (Brantley et al., 2008). This supposition is supported by mineralogical data for a number of these
locations that indicate a lack of plagioclase throughout the regolith and the biggest relative change in plagioclase concentration at the saprolite-rock interface (Buss et al., 2008; Oh and Richter, 2005; Schroeder et al., 2002; White et al., 1998, 2001). The abrupt weathering front is equivalent to depletion profiles in the “local-equilibrium” regime modeled by Lebedeva et al. (2010) to occur at physical erosion rates below 0.002 mm yr\(^{-1}\) (in agreement with rates of ~0.0008 mm yr\(^{-1}\) observed here), and equivalent to locations with strong erosion-limitation of total denudation. Further, as discussed later, Na loss and weathering rates in these locations appear somewhat disconnected from modern climate forcing. The exact regolith residence time in these landscapes is difficult to constrain. However, the depth of regolith and low physical erosion rates suggest landscapes with mean residence times ≥ 10\(^6\) yr. Thus, ample time for Na loss and exposure to paleoclimate variation may account in part for the degree of depletion noted in these profiles.

The exception to this pattern among the fully Na depleted locations is the Luquillo profile, that has a physical erosion rate of ~95 g m\(^{-2}\) yr\(^{-1}\), equivalent to 0.036 mm yr\(^{-1}\), and extreme climate forcing of 4200 mm yr\(^{-1}\) of precipitation and mean annual temperature of 22 °C (Table 1). Note that the physical erosion rate calculated here is greater than that estimated by Riebe et al. (2003) and roughly equivalent to \(D_{\text{CRN}}\), a result of referencing physical erosion to Zr concentration to the soil-saprolite interface rather than the protolith (Eq. 4). These data indicate nearly all of the chemical weathering at this location occurs in the saprolite, as expected since no fieldspar remains above the rock-saprolite interface, and that denudation over the cosmic-ray penetration depth is dominated by physical erosion. It thus appears the intense climate forcing at this location allows the Na chemical weathering advance rate and Na depletion to keep pace with and/or exceed physical erosion in a near steady-state condition. This facilitates development of a fully Na depleted profile, while still maintaining what has been reported as one of the fastest chemical weathering granitic sites in the world (White and Blum, 1995). The low erosion site and Luquillo data suggest two possible forms of erosion-limited systems, those limited strictly by very low erosion rates (less than 20 g m\(^{-2}\) yr\(^{-1}\)) such that regolith thickness increases and no steady state is maintained, and those where chemical weathering is fast enough to keep pace with physical erosion in a steady-state condition.

The remaining locations with physical erosion rates greater than 20 g m\(^{-2}\) yr\(^{-1}\) were separated according to climate as quantified by the humidity index (Figure 1b and c). The energy-limited locations (HI>1) exhibited only partial Na depletion throughout the regolith profiles, and regolith profiles up to two orders of magnitude shallower than the low erosion locations. In addition, the energy-limited Na depletion profiles presented a more gradual decline in Na depletion with increasing depth, roughly exponential in shape. This partial Na depletion indicates plagioclase persists into surface soils, suggesting that the active weathering front extends through the entire regolith profile (Williams et al., 2010). Furthermore, the average \(\tau_{\text{Na}}\) tended to increase with mean annual temperature, suggesting a possible role for temperature as a kinetic constraint on Na mass loss in these locations (discussed in detail later).

The water-limited locations (HI<1) exhibited very shallow, partially depleted Na profiles (Figure 1c). The \(\tau_{\text{Na}}\) tended to decrease linearly with depth, which similar to the energy-limited locations, indicates the active weathering front extends through the entire regolith depth. In addition, these locations trended towards increasing Na depletion with increasing MAP, suggesting water limitation as a potential kinetic limit to Na weathering and mass loss.

3.2. Surface Na depletion and environmental variables

The \(\tau_{\text{Na}}\) values at the soil surface, which varied widely among locations, provide a proxy for depletion profile development that may be directly compared with environmental variables (Williams et al., 2010) (Figure 2). Comparing these data with the humidity index indicated strong correlation of annual water balance to surface Na depletion for the majority of locations, with an exponential decrease in \(\tau_{\text{Na}}\) with increasing water availability, except for locations with MAT<5 °C and those with a physical erosion rate <20 g m\(^{-2}\) yr\(^{-1}\) (Figure 2a). This general pattern corroborates a number of soil geochemical studies on various rock types documenting linear to threshold type trends of cation depletion with increasing precipitation and water availability (Chadwick et al., 2003; Driese et al., 2005; Rasmussen and Tabor, 2007; Sheldon et al., 2002).

The grouping of energy-limited locations that do not follow the trend of increasing Na loss with increasing water availability all have mean annual temperature of less than 5 °C. The lack of Na depletion in these locations is similar to pedogenic thresholds noted at the boundary between rain and snow-dominated ecosystems in the Sierra Nevada of California. The threshold differences in soil properties noted in those studies were proposed to be a function of both temperature limits on chemical weathering, and the complex effects of snow hydrology and loss of mean annual precipitation to

### Table 1

<table>
<thead>
<tr>
<th>Site Category*</th>
<th>MAP((\text{mm yr}^{-1}))</th>
<th>MAT(^{(\circ}\text{C}))</th>
<th>HI* (Unitless)</th>
<th>(\tau_{\text{Na, CRN}}) ((\text{g m}^{-2} \text{yr}^{-1}))</th>
<th>E(^{88}) (g m(^{-2}) yr(^{-1}))</th>
<th>(D_{\text{Na, total}}) ** (mol Na m(^{-2}) yr(^{-1}))</th>
<th>(W_{\text{Na, total}}) *** (mol Na m(^{-2}) yr(^{-1}))</th>
<th>(M_{\text{Na, flux}}) †† (mol Na m(^{-2}) yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully depleted</td>
<td>(n=2)</td>
<td>1140±100</td>
<td>13.0±3.6</td>
<td>1.36±0.07</td>
<td>0.95±0.03</td>
<td>15.1±2.15</td>
<td>9.8±6.5</td>
<td>0.015±0.004</td>
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<tr>
<td>Luquillo***</td>
<td>(n=1)</td>
<td>5620</td>
<td>22.0</td>
<td>2.95</td>
<td>-1.00</td>
<td>177.0</td>
<td>95.0</td>
<td>0.19</td>
</tr>
<tr>
<td>Partially depleted, energy-limited</td>
<td>(n=7)</td>
<td>798±59</td>
<td>6.8±1.4</td>
<td>1.48±0.20</td>
<td>-0.43±0.06</td>
<td>1145±8.07</td>
<td>84.8±7.2</td>
<td>0.108±0.011</td>
</tr>
<tr>
<td>Partially depleted, water-limited</td>
<td>(n=9)</td>
<td>500±27</td>
<td>16.4±0.5</td>
<td>0.56±0.04</td>
<td>-0.31±0.04</td>
<td>77.6±8.8</td>
<td>56.3±3.8</td>
<td>0.081±0.013</td>
</tr>
</tbody>
</table>

* Site category refers to the relative surface Na depletion with depleted sites defined as those with surface \(\tau_{\text{Na}}<0.80\) and enriched defined as those with surface \(\tau_{\text{Na}}>0.80\). The energy-limited and water-limited categories refer to sites with humidity index greater than and less than 1, respectively.

† Mean annual precipitation.

‡ Mean annual temperature.

§ Humidity index calculated as the ratio of mean annual precipitation to potential evapotranspiration.

** Mass transfer coefficient for Na averaged over the depth of cosmogenic nuclide penetration. Values calculated following Anderson et al. (2002) and using Zr as the immobile element.

*** Total regolith denudation rate calculated following Dixon et al. (2009a,b) (see Eq. [3] in text).

**** Physical erosion rate calculated following Dixon et al. (2009a): \(E = D_{\text{CRN}}(C_{Zr, sap}/C_{Zr, soil})\), where \(C_{Zr, soil}\) is the average Zr concentration in soil horizons.

#### Notes:

1. Total regolith denudation rate calculated following Dixon et al. (2009a,b) (see Eq. [3] in text).
2. Physical erosion rate calculated following Dixon et al. (2009a): \(E = D_{\text{CRN}}(C_{Zr, sap}/C_{Zr, soil})\), where \(C_{Zr, soil}\) is the average Zr concentration in soil horizons.
3. Total regolith Na weathering rate calculated as a fraction of \(D_{\text{Na, total}}\) based on \(\tau_{\text{Na, CRN}}\) (see Eq. [4] in text).
4. Regolith integrated mass flux of Na based on depth profiles of \(\tau_{\text{Na}}\), horizon depth, and bedrock density (see Eq. [2] in text).
5. Data for the hot, wet Puerto Rico location was not included in the fully depleted category in order to highlight the differences in Na loss and physical erosion rates.
and $y=y_{o}-ax^{2}$, fit between surface $\tau_{Na}$ and humidity index where $y_{o}=0.34$, $a=-0.87$ and $b=0.39$ ($r^{2}=0.86$). The function was fit excluding the wet locations with MAT $<5$ °C, and locations with physical erosion rate ($E$) $>20$ g m$^{-2}$ yr$^{-1}$.

Surface $\tau_{Na}$ values also generally increased with increasing physical erosion rate (Figure 2c), i.e., decreasing extent of surficial Na depletion with increasing erosion rate, similar to numerical model results of Ferrier and Kirchner (2008) and Lebedeva et al. (2010). In general, energy-limited locations exhibited greater surface Na depletion than water-limited locations at an equivalent physical erosion rate, except for the energy-limited locations with MAT $<5$ °C that plot with the water-limited locations (Figure 2c). Note that the Luquillo profile exhibited complete Na depletion at moderate erosion rates, likely a result of intense climate forcing and Na loss in saprolite layers (White et al., 1998). Indeed, as indicated by other locations with similar physical erosion rates as Luquillo, surface Na depletion tended to increase from water-limited to energy-limited locations with Luquillo as the fully depleted energy-limited end-member (Figure 2c) with a similar trend noted in Figure 2a. The locations with fully depleted Na profiles, surface soil $\tau_{Na}\approx-1$ and physical erosion rate less than 20 g m$^{-2}$ yr$^{-1}$, did not exhibit any clear relationship between surface $\tau_{Na}$ and water availability or temperature. As noted previously, near complete Na depletion occurs in these profiles in saprolite layers at depths greater than $\sim$2 m, such that surface profile Na depletion would not necessarily be expected to exhibit trends with modern climate forcing.

The climate-erosion interaction control on Na depletion thus appears to be non-linear, with an overall exponential trend of increasing Na depletion with increasing water availability. This trend is overlain by thresholds or abrupt transitions in Na depletion that occur at erosion rates less than 20 g m$^{-2}$ yr$^{-1}$ (transition to complete Na depletion and deep profiles), and mean annual temperature less than 5 °C (minimal Na depletion and shallow profiles relative to locations with equivalent water availability and erosion rate).

### 3.3. Regolith depth and Na mass loss

Total regolith Na mass loss ($M_{Na_{regolith}}$) exhibited a clear break relative to surface Na depletion, increasing abruptly in a threshold type function from an average loss of 349±77 mol Na m$^{-2}$ (± standard error) in sites with surface $\tau_{Na}$ values greater than $-0.8$, to an average loss of 19,112±2990 mol Na m$^{-2}$ for sites with $\tau_{Na}\approx-1$ (Figure 3). This threshold corresponds with an order of magnitude increase in regolith depth from $49\pm9$ cm to $856\pm182$ cm at the transition to locations with physical erosion less than 20 g m$^{-2}$ yr$^{-1}$ (Table A1). It appears that substantial chemical Na mass loss is primarily associated with low erosion locations and Na depletion profiles that resemble modeled profiles for erosion-

Fig. 2. Surface horizon sodium mass transfer coefficient ($\tau_{Na}$) relative to [A] humidity index defined as mean annual precipitation divided by potential evapotranspiration, [B] mean annual temperature (MAT), and [C] physical erosion rate. Open triangles and filled squares represent sites with a humidity index less than and greater than 1, respectively. Luquillo is noted as the black square. The dashed line in [A] is the function: $y=y_{o}-ax^{2}$, fit between surface $\tau_{Na}$ and humidity index where $y_{o}=0.34$, $a=-0.87$ and $b=0.39$ ($r^{2}=0.86$). The function was fit excluding the wet locations with MAT $<5$ °C, and locations with physical erosion rate ($E$) $>20$ g m$^{-2}$ yr$^{-1}$.

Fig. 3. Regolith depth relative to [A] physical erosion rate, and [B] the time-integrated total regolith Na mass loss ($M_{Na_{regolith}}$) relative to surface horizon sodium mass transfer coefficient ($\tau_{Na}$). The open triangles and filled squares represent sites with a humidity index less than and greater than 1, respectively. Luquillo is noted as the black square.
limited systems (Lebedeva et al., 2010). These authors also noted that erosion-limited sites with fully depleted profiles were parametrically unstable in their numerical model, such that small variations in extrinsic variables such as climate and erosion manifested as orders of magnitude variation in regolith depth and mass loss. This may account for the large variance in depth and mass flux noted here for such locations.

The shallow, partially Na-depleted profiles were characterized by physical erosion rates on the order of 74±11 g m⁻² yr⁻¹, equivalent to 0.028±0.004 mm yr⁻¹, suggesting even in the presence of moderate rates of physical mass removal, Na chemical mass loss may be minimized (Table 1). The moderate physical erosion rate and shallow regolith at these locations suggest regolith mean residence times on the order of 10⁴ to 10⁵ yr such that relatively short mineral residence time may limit the contribution of Na chemical mass loss to total Na denudation (White and Brantley, 2003; Yoo and Mudd, 2008). Further, grouping these data according to energy- and water-limited climate regimes indicated significantly greater Na mass loss in energy-limited sites (589±138 mol Na m⁻²) relative to water-limited locations (190±30 mol Na m⁻²) (Table 1). The limited range and magnitude of Na mass loss in the water-limited sites implicates negative annual water balance as a key climate parameter for predicting Na mass loss in landscapes of moderate erosion rate.

3.4. Erosion and kinetic limits on Na chemical weathering

We directly examined the notion of erosion- and kinetic-limited weathering rate regimes by comparison of Na chemical weathering rate calculated using Eq. (4) to total Na denudation rate (Figure 4). Data plotting near the 1:1 line indicate dominance of total Na denudation by chemical weathering and erosion-limited regimes, whereas data plotting below this line indicate increasing dominance of Na denudation by physical erosion and a transition to kinetic-limited regimes. In accord with the form of Eq. (4), sites with τNa−Na/τEa−Na≈1 fell close to the 1:1 line, indicating chemical weathering dominates Na denudation, and supporting the hypothesis that these sites are strongly erosion-limited as suggested by Na depletion profiles and the numerical modeling results of Lebedeva et al. (2010). The remaining data trend towards increasing kinetic limitation with the majority of both energy- and water-limited climate locations plotting near or below the transitional regime reference line with a slope of 0.5. When grouped according to humidity index, energy-limited sites exhibited a slope of 0.45 suggesting sites dominantly in the transitional weathering regime, whereas, water-limited locations exhibited a slope of 0.11 suggesting dominantly kinetic-limited conditions. Importantly, the water-limited locations with the greatest total Na denudation rate were the most arid, with humidity index less than 0.45, and exhibited the greatest discrepancy between WNa-total and DNa-total. These sites exhibited positive subsurface τNa values (Figure 1b) suggesting dust accumulation may in part drive the decoupling of chemical weathering and total Na denudation for the most arid locations (Ewing et al., 2006).

The data were further analyzed using the empirical function: 

\[ W_{Na-total} = α(D_{Na-total})^β \exp(-Ea/RT \cdot MAP) \]

Fitting this function stepwise to the entire dataset indicated strong and significant (r²=0.85; P<0.0001) coupling of Na chemical weathering rate to total Na denudation rate (A=0.81±0.10), and precipitation (γ = 0.69±0.13), and surprisingly no significant relation to temperature (analysis discussed later suggests temperature influence may be masked when the data are analyzed as a single dataset). These values suggest total Na denudation as a dominant constraint on Na weathering rate and erosion-limited systems, with second order constraint of precipitation. The lack of a significant relation to temperature was surprising given that previous field-based regolith and watershed studies have noted moderate to strong control of temperature on weathering rates, with Ea for Na on the order of 15 to 109 kJ mol⁻¹ (Riebe et al., 2004; Velbel, 1993; White and Blum, 1995; Williams et al., 2010). The lack of temperature significance in the mixed linear model indicates that overall, total Na denudation and precipitation are the dominant controls on Na chemical weathering. However, single linear regression analysis of total Na weathering rate and temperature, with data separated by energy- and water-limited sites, did indicate significant correlation of weathering rate to temperature, with sodium Ea equivalent to 69±15 kJ mol⁻¹ Na for energy-limited locations, and 136±64 kJ mol⁻¹ Na for water-limited locations (Figure 5). Therefore, temperature is correlated with chemical weathering, but the temperature dependence can only be discerned with careful analysis of subsets of data. Discrepancies in the literature where researchers either see a temperature dependence (White and Blum 1995; White et al., 1999) or do not see such a dependence (Huh and Edmond, 1999) may be related to this observation.

Solubility and kinetics control the rates of chemical weathering of albite in eroding systems. Lebedeva et al. (2010) demonstrated that both Ea and ΔH, the reaction enthalpy, for albite dissolution can

![Fig. 4. Total sodium weathering rate (WNa-total) relative to Na supply rate (DNa-total) defined as parent rock Na concentration (mol M⁻¹) times the total denudation rate [M L⁻² t⁻¹] and B relative to physical erosion rate. Open triangles and filled squares represent sites with a humidity index less than and greater than 1, respectively. Luquillo is noted as the black square. The solid line is the 1:1 fit between WNa-total and DNa-total and represents the erosion-limited weathering regime end-member. The dashed line is fit with a slope of 0.5 and represents the midpoint transitional zone between erosion- and kinetic-limited weathering regimes. The dash-dot line is fit with a slope of zero and represents the kinetic-limited regime end-member.](image)

![Fig. 5. Arhenius plot of the natural log of total sodium weathering rate (WNa-total) relative to the inverse of mean annual temperature (MAT). Open triangles and filled squares represent sites with a humidity index less than and greater than 1, respectively. Luquillo is noted as the black square. The solid line is fit to the energy-limited locations and the dash-dot line is fit to the water-limited sites. Note that the Panola and Davis Run locations that exhibited strong erosion-limited Na chemical weathering rates are not included with the energy-limited locations.](image)
appear in the equations describing weathering rate temperature
dependence. Specifically, according to their calculations for a
simplified model granite, the apparent activation energy inferred
from an Arrhenius function should equal \( nE_a + \Delta H \) \( (n = 0.5 \) or \( 1) \)
under kinetic limitation, but should equal \( \Delta H \) under erosion-
limitation. According to laboratory measurements of albite weathering,
\( E_a \approx 60 \text{ kJ mol}^{-1} \) and \( \Delta H \approx 80 \text{ kJ mol}^{-1} \) \( (\text{Johnson et al., 1992}) \).
The energy-limited site \( E_a \) is thus comparable to albite \( \Delta H \) under
laboratory conditions and therefore suggestive of erosion-limited
rates, whereas the water-limited \( E_a \) is comparable to \( E_a + \Delta H \)
suggesting kinetic-limited rates. The apparent activation energy
data agree with the location of energy-limited locations in the
erosion- to transitional regime, and the water-limited data in the
transitional to kinetic-limited regime in Figure 4.

The apparent kinetic limitation in the water-limited locations is
most likely related to generally dry conditions. These locations have
mean annual temperature greater than 14 °C, annual precipitation
less than 600 mm yr\(^{-1}\), and a humidity index less than 0.6, all of
which point towards water availability and negative annual water
balance as the dominant climatic factor limiting Na chemical
weathering rate. Locations with negative annual water balance likely
exhibit insufficient water for removal of weathering products
\( (\text{Amundson, 2005; Arkley, 1963; Harden, 1990}) \) in combination
with short water residence time due to high evapotranspirative
demands that may concentrate soil solutes and thereby reduce
with short water residence time due to high evapotranspirative

depth and Na depletion increased
subsets of data as shown in Figure 4. However, the data
also indicate thresholds and marked nonlinear transitions in the
religion depletion parameters to water availability according to erosion rate and mean annual temperature.

The most pronounced transition occurs for locations with physical
erosion rates less than 20 g m\(^{-2}\) yr\(^{-1}\) that abruptly transition to very
deep, fully Na depleted regolith profiles with very low chemical
weathering rates, and well defined Na weathering fronts at the
saprolite-rock boundary. These properties appear to be somewhat
independent of climate parameters in that near complete Na
deposition occurs deep in the regolith at the saprolite-rock interface
and indicates chemical weathering rates that are strongly erosion-
limited and possibly not in steady-state with modern climate forcing.
The exception to this pattern was the Luquillo profile that exhibited
the fastest Na chemical weathering rate in this dataset, yet exhibits a
fully Na depleted regolith profile with the weathering front at the
saprolite-rock interface. Luquillo also has an intense climate forcing
with over 4 m of annual precipitation and mean annual temperature
greater of 22 °C coupled with a physical erosion rate that is an order of
magnitude greater than the other fully Na depleted profiles. Researchers have argued that regolith formation and loss to erosion
are in steady-state, perhaps consistent with the analysis here. It
appears that for this location, the intense climate forcing facilitates
maintenance of the weathering advance rate, and thus chemical
weathering rate, in near steady-state with physical erosion.

The remaining data with erosion rates greater than 20 g m\(^{-2}\) yr\(^{-1}\)
separated according to annual water balance and mean annual temperature. Regolith profile depth and Na depletion increased
continuously with increasing water availability, with poorly defined
weathering fronts that extend throughout the entire regolith. In the
energy-limited (positive annual water balance) locations, Na chemical
weathering rates were dominantly erosion-limited or in a transitional
regime grading towards kinetic limitation, with second order constraint
of temperature that manifested as Na apparent activation energy of
69 kJ mol\(^{-1}\) Na. The water-limited (negative annual water balance)
locations exhibited very shallow regolith profiles, limited Na depletion,
chemical weathering rates only weakly related to total Na denudation,
and apparent Na activation energy of 136 kJ mol\(^{-1}\) Na, possibly
showing functional dependence upon both the activation energy and
\( \Delta H \) of feldspar dissolution. These data are suggestive of water
availability induced kinetically limited weathering regimes.

The generalized empirical patterns described here correspond well
with numerical model results of \( \text{Ferrier and Kirchner (2008) and} \)
\( \text{Lebedeva et al. (2010}) \) that effectively summarize the nonlinear
dependence of chemical weathering on physical erosion and the effect of
physical erosion on relative Na depletion profile form and depth.
However, we also noted deviations from modeled results that
highlight the important role climate plays in moderating Na
weathering and mass loss. In particular, the hot, wet Luquillo profile exhibited a fully Na depleted regolith profile at moderate physical erosion rates, whereas other locations with similar physical erosion
but less intense climate forcing exhibited minimal Na depletion. Other
sites that deviate from previous model results include those that are
strongly water-limited with humidity index of <0.5, and those that are
energy-limited with a mean annul temperature less than 5 °C.

Previous modeling and empirical analyses of weathering rates have
largely described the climate–erosion–weathering interaction as a
continuous function. The synthesis presented here indicates that
uniform treatment of this interaction across climate and erosional
regimes masks key thresholds and transitions in plagioclase weathering
and regolith Na loss. These data thus provide a basis for refining regolith
formation models in order to capture the observed transitions in Na
deposition, mass loss and chemical weathering rate.

Supplementary materials related to this article can be found online

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References

Weathering and Soils : Treatise on Geochemistry, Elsevier, Amsterdam, pp. 1–35.
Coupling between biota and earth materials in the Critical Zone. Elements 3 (5),
227–232.
analysis, and rates of solute loss: linkages between weathering and erosion in a


