

doi:10.1016/S0016-7037(03)00382-X

### Long-term rates of chemical weathering and physical erosion from cosmogenic nuclides and geochemical mass balance

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(Received February 12, 2003; accepted in revised form May 28, 2003)

Abstract—Quantifying long-term rates of chemical weathering and physical erosion is important for understanding the long-term evolution of soils, landscapes, and Earth's climate. Here we describe how long-term chemical weathering rates can be measured for actively eroding landscapes using cosmogenic nuclides together with a geochemical mass balance of weathered soil and parent rock. We tested this approach in the Rio Icacos watershed, Puerto Rico, where independent studies have estimated weathering rates over both short and long timescales. Results from the cosmogenic/mass balance method are consistent with three independent sets of weathering rate estimates, thus confirming that this approach yields realistic measurements of long-term weathering rates. This approach can separately quantify weathering rates from saprolite and from overlying soil as components of the total. At Rio Icacos, nearly 50% of Si weathering occurs as rock is converted to saprolite; in contrast, nearly 100% of Al weathering occurs in the soil. Physical erosion rates are measured as part of our mass balance approach, making it particularly useful for studying interrelationships between chemical weathering and physical erosion. Our data show that chemical weathering rates are tightly coupled with physical erosion rates, such that the relationship between climate and chemical weathering rates may be obscured by site-to-site differences in the rate that minerals are supplied to soil by physical erosion of rock. One can normalize for variations in physical erosion rates using the "chemical depletion fraction," which measures the fraction of total denudation that is accounted for by chemical weathering. This measure of chemical weathering intensity increases with increasing average temperature and precipitation in data from climatically diverse granitic sites, including tropical Rio Icacos and six temperate sites in the Sierra Nevada, California. Hence, across a wide range of climate regimes, analysis of chemical depletion fractions appears to effectively account for site-to-site differences in physical erosion rates, which would otherwise obscure climatic effects on chemical weathering rates. Our results show that by quantifying rates of physical erosion and chemical weathering together, our mass balance approach can be used to determine the relative importance of climatic and nonclimatic factors in regulating long-term chemical weathering rates. Copyright © 2003 Elsevier Ltd

### 1. INTRODUCTION

Chemical weathering of minerals supplies nutrients and solutes to soils, streams and the oceans and is thus an important component in many biogeochemical cycles. For example, silicate weathering modulates ocean alkalinity and thus is the dominant long-term sink for atmospheric CO<sub>2</sub> and the dominant regulator of the greenhouse effect over geologic timescales. Hence, to the extent that chemical weathering rates increase with temperature, weathering feedbacks should, over millions of years, buffer Earth's climate against large temperature shifts (e.g., Berner et al., 1983). However, chemical weathering rates may be coupled with physical erosion rates (Stallard and Edmond, 1983; Gaillardet et al., 1999; Riebe et al., 2001), as well as climate, such that Earth's long-term climatic evolution may also be affected by tectonic forcing of physical erosion rates (Raymo et al., 1988). If chemical weathering rates are highly sensitive to the availability of fresh mineral surfaces (which would tend to be enhanced by increased physical erosion rates), periods of increased erosion (due to changes in uplift rates or climate) would be marked by global cooling, due to increased atmospheric  $CO_2$  consumption by weathering (Raymo et al., 1988). As this example illustrates, a comprehensive view of chemical weathering in global biogeochemical cycles requires a better quantitative understanding of the coupling between chemical weathering and physical erosion. Because chemical weathering and physical erosion also interact to generate soils and sculpt landscapes, quantifying them together over the long timescales of soil formation is also important for quantitative study of soil development and landscape evolution.

Long-term chemical weathering rates have typically been measured using soil mass-balance techniques (e.g., April et al., 1986), which quantify the total mass that is removed when a specified volume of unweathered parent material is converted to soil (Brimhall and Dietrich, 1987). If physical erosion has been negligible, mass loss from a soil can be attributed to chemical weathering alone. In that case, the mass loss can be interpreted as a chemical weathering rate, using the soil's age (if known) to average the loss over the time since the soil began to form (e.g., Bain et al., 1993; Taylor and Blum, 1995). But noneroding soils of known age are rare, and by their nature preclude comparisons of physical erosion and chemical weathering (because they require erosion to be negligible). In eroding landscapes, soil age is difficult to define because soils are

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continually renewed as fresh material is incorporated from below and replaces the weathered material that is removed from the surface by physical erosion. Instead of having ages, eroding soils have average residence times, which can be used together with mass losses to infer chemical weathering rates (White et al., 1998; Anderson et al., 2002). However, conventional methods for estimating residence times for eroding soils often yield uncertainties that are large (Anderson et al., 2002) or difficult to quantify (White et al., 1998). Hence, few estimates of long-term chemical weathering rates are available for comparison with long-term physical erosion rates.

However, measurements of long-term physical erosion rates are now widely available from cosmogenic nuclide methods; cosmogenic nuclide concentrations in saprolite, rock, soils and alluvial sediment can be used to infer long-term rates of soil production (Heimsath et al., 1997), outcrop erosion (Lal, 1991), soil denudation (Small et al., 1999), and catchment denudation (Brown et al., 1995; Bierman and Steig, 1996; Granger et al., 1996; Riebe et al., 2000; Kirchner et al., 2001; Schaller et al., 2001).

Here we show how cosmogenic nuclide and geochemical mass balance methods can be applied together to measure long-term chemical weathering rates of eroding catchments and soils. Our mass balance approach (Kirchner et al., 1997; Riebe et al., 2001) combines long-term denudation rates, inferred from cosmogenic nuclides in soils and sediment, with dissolution losses, inferred from the rock-to-soil enrichment of insoluble elements. It differs from the traditional mass balance approach for measuring long-term weathering rates (April et al., 1986; Brimhall et al., 1991; Anderson et al., 2002) in that it explicitly accounts for physical erosion, making it widely applicable in eroding landscapes. Because long-term physical erosion rates are calculated as part of the approach, it is useful for quantifying how chemical weathering and physical erosion interrelate over the long timescales of soil formation.

We tested our approach in the Rio Icacos watershed, Puerto Rico, where independent studies have estimated weathering rates over both short and long timescales (McDowell and Asbury, 1994; White et al., 1998). Our weathering rate measurements are consistent with three independent sets of weathering rate data, thus confirming that our technique yields realistic estimates of long-term weathering rates. Our approach can be used to separately quantify weathering rates from saprolite and overlying soil as parts of the total, and thus can identify patterns of weathering within regolith profiles. We compare our results from tropical Rio Icacos with earlier work from a series of drier, cooler sites (Riebe et al., 2001) and show that the relationship between climate and chemical weathering rates may be obscured by site-to-site differences in physical erosion rates (Riebe et al., 2001; Anderson et al., 2002), even when weathering rates of extreme tropical climates are considered alongside those of milder, temperate sites. Climatic effects on chemical weathering emerge more clearly when chemical weathering rates of our catchments are normalized by their total denudation rates, to yield "chemical depletion fractions." Across our sites, chemical depletion fractions are insensitive to variations in physical erosion rates, and increase with increasing precipitation and temperature, effectively accounting for mineral supply effects due to site-to-site differences in physical erosion rates, which would otherwise obscure the relationships



Fig. 1. Map showing location of Rio Icaco, Puerto Rico (inset), and sampling locations within the study area. Closed circles mark locations of cosmogenic nuclide samples of stream sediment. Three cosmogenic nuclide samples were also collected from soil surfaces within subcatchments RI-1 and RI-4. Light gray lines are streams, thick gray lines are catchment boundaries of Rio Icacos (RI-6) and Rio Sabana (RI-8) samples, and thin black lines are catchment boundaries of smaller subcatchments RI-1, 2, 4 and 7, where we sampled widely distributed rocks and soils for bulk chemical analysis. Open circles in RI-4 and RI-7 are locations of profiles sampled by hand auger (see text). Star on south ridge of RI-1 marks profile sampling location of White et al. (1998).

between climate and chemical weathering rates. Our results indicate that, by quantifying rates of physical erosion and chemical weathering together, the mass balance approach can be used to provide a rational framework for determining the relative importance of climatic and nonclimatic factors in regulating long-term chemical weathering rates.

### 2. FIELD SITE

The upper reaches of Rio Icacos, its tributaries, and the adjacent slopes lie within the Luquillo Experimental Forest of Puerto Rico (Fig. 1). Rio Icacos has long been the site of diverse geochemical, hydrological, biologic, and geomorphological research, including studies of physical erosion by land-sliding and other processes (e.g., Larsen and Simon, 1993; Larsen, 1997; Larsen et al., 1999), long-term denudation rates from cosmogenic nuclides (Brown et al., 1995, 1998), and chemical weathering rates (McDowell and Asbury, 1994; Stonestrom et al., 1998; White et al., 1998).

Our goal was to compare chemical weathering rates inferred from cosmogenic nuclides and geochemical mass balance with results from conventional approaches for measuring chemical weathering rates. Rio Icacos is an ideal location for such a comparison because chemical weathering rates have been inferred from three independent sets of data, spanning both short and long timescales: stream solute fluxes from water samples collected at the Rio Icacos gauge (McDowell and Asbury, 1994; White and Blum, 1995), solute concentrations and infiltration rates of regolith pore water (Stonestrom et al., 1998;

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White et al., 1998), and bulk chemical losses from a regolith profile (White et al., 1998).

For our measurements of rates of chemical weathering and physical erosion, we selected 3 tributary catchments above the Rio Icacos gauge and one tributary just outside the gauged area (Fig. 1). Among our catchments are the two main forks of the Quebrada Guaba (Fig. 1); the more southerly fork includes the regolith profile site of (White et al., 1998), thus facilitating direct comparisons with weathering rates that they measured. Earlier work on the Quebrada Guaba also quantified cosmogenic nuclide concentrations in stream-borne quartz (Brown et al., 1998).

Our catchments are small and steep, with deeply incised channels, average hillslope gradients of 0.48 to 0.67, and slopes that taper into relatively gentle convex crests at 700 to 750 m altitude. Catchment relief ranges from 100 to 150 m. Lower montane, wet colorado forests are the dominant vegetative cover; mean annual temperature is 22 °C and average annual rainfall is 420 cm/yr, coming mostly from tropical depressions, storms, and hurricanes carried by easterly Caribbean trade winds. Landslides, occurring mainly as shallow soil slips and debris flows, are triggered by long, intense rainfall events (Larsen and Simon, 1993), and are the dominant geomorphic agents at Rio Icacos, accounting for approximately 90% of the estimated sediment transport from slopes (Larsen, 1997). Other important hillslope sediment transport processes include slope wash, tree throw and soil creep (Larsen et al., 1999), which together appear to dominate sediment transport on gentle ridgetops and on slopes that have not been subjected to recent landslides.

Rio Blanco quartz diorite underlies the Rio Icacos headwaters everywhere except in a small area along the eastern divide, where volcanic bedrock is common near the ridgetop (Briggs, 1973; Seiders, 1974). Our catchments are developed in guartz diorite, along the river's western divide (Fig. 1). Our aim was to characterize chemical weathering from the dominant Rio Icacos rock type, and also stay within a single, roughly homogeneous lithology. On Rio Icacos slopes, the quartz diorite weathers to an oxidized, highly friable saprolite, which retains much of the bedrock's physical structure and can reach depths of up to 8 m (White et al., 1998). Intense weathering at the saprolite-rock boundary almost completely converts plagioclase (the dominant mineral in the rock), K-feldspar, and hornblende to secondary minerals (Fig. 2), thereby releasing nearly all of the rock's Ca and Na into solution (White et al., 1998). Intense weathering and alteration of minerals continues as they are exhumed to hillslope surfaces, as indicated by increasingly abundant epitaxial kaolinite on biotite (Murphy et al., 1998) and etch pits on quartz (Schulz and White, 1999) with decreasing depth in saprolite. Nevertheless, coherent corestones (typically 1-2 m in diameter) occasionally survive exhumation through saprolite to crop out on hillslope surfaces. Saprolite is overlain by 50-150 cm of soil, which grades from an orange or mottled-orange, clay-rich, basal B horizon to a thin (5-10 cm), organic-rich A horizon. Abundant earthworm casts, blowndown trees with soil-rich root wads, and a lack of strong horizonation within the basal soil together indicate that the B horizon is well mixed by tree throw and bioturbation.

In the next section, we explain how we used the bulk chemical composition of soils, saprolite and rock, along with



Fig. 2. Mineral abundance versus depth for plagioclase (triangles), quartz (diamonds), and kaolinite (crosses) from the study of White et al. (1998) of regolith along the southern ridge of Quebrada Guaba (see Fig. 1 for location). The absence of plagioclase and appearance of kaolinite in saprolite suggests intense weathering occurs at the saprolite-rock boundary, and implies that most of the rock's Ca and Na are released into solution there.

cosmogenic nuclide concentrations in soil and sediment, to measure long-term rates of physical erosion and chemical weathering for Rio Icacos. We then compare results from our technique with independent estimates of chemical weathering rates from previous work at the site (McDowell and Asbury, 1994; Stonestrom et al., 1998; White and Blum, 1998).

### 3. MASS BALANCE APPROACHES FOR MEASURING LONG-TERM CHEMICAL WEATHERING RATES

### 3.1. Theory

Long-term chemical weathering rates have typically been inferred using a mass balance approach (April et al., 1986; Brimhall and Dietrich, 1987), in which chemical weathering outputs are inferred from the changes wrought in parent material as it is converted to weathered soil. In the mass balance approach, chemical weathering losses are estimated from measurements of immobile element enrichment in the weathered material. Elements that are immobile during chemical weathering become enriched as other elements are removed by dissolution; the greater the mass lost through dissolution, the greater the relative enrichment of the immobile elements that are left behind.

# 3.2. Chemical Weathering Rates from Noneroding Soils of Known Age

If physical erosion from a soil has been negligible, as may be the case on some flat-topped moraines (Taylor and Blum, 1995) and fluvial terraces (Bain et al., 1993), mass losses can be attributed to chemical weathering alone. If so, measurements of immobile element enrichment yield estimates of mass loss that can be interpreted as chemical weathering rates using soil ages, assuming they can be quantified. Soil ages provide rate con-



Fig. 3. Schematic showing mass balances of soluble (A) and insoluble (B) soil components. (A) Soil production is balanced by removal due to physical erosion (E) and chemical weathering (W), and is equal to the total denudation rate (D), so soil depth (h) is constant. (B) Inputs from soil production are balanced solely by outputs from physical erosion for immobile elements such as zirconium.

stants for averaging total mass losses from weathering over time, thus yielding long-term average chemical weathering rates. However, because erosion must be negligible, this approach is not useful for determining the extent to which rates of physical erosion and chemical weathering are interrelated. Hence, although rates of fresh mineral supply (e.g., Lee et al., 1998; Nugent et al., 1998) and thus physical erosion (Stallard and Edmond, 1983) are thought to significantly affect chemical weathering rates, the linkage between them has remained speculative in the absence of colocated measurements of long-term rates of chemical weathering and physical erosion. Moreover, because noneroding soils of known age are rare, conventional soil mass balance methods cannot be widely applied, and have yielded few measurements of long-term chemical weathering rates.

# 3.3. Chemical Weathering Rates from Eroding Landscapes

In mountainous settings, most soils have substantial physical erosion rates. In soils undergoing steady-state erosion, the enrichment of immobile elements can still provide a measure of the total mass lost due to chemical weathering, just as it does in a noneroding soil. But in eroding landscapes, soil age is difficult to define, because soil is continually renewed as fresh rock is incorporated from below, replacing weathered soil removed by physical erosion at the surface. In soils undergoing such denudation, cosmogenic nuclides can be used to measure rates of denudation and chemical weathering, as we show below.

### 3.3.1. Relationship between immobile element enrichment and chemical weathering rate for eroding soils

For a soil undergoing steady-state formation, erosion, and weathering (such that the mass of weathered material in storage on the landscape is approximately constant through time), conservation of mass (Fig. 3A) implies that the rate of conversion from parent material to weathered products will be equal to the total denudation rate, which in turn will equal the sum of the rates of chemical weathering and physical erosion:

$$\mathbf{R} = \mathbf{D} = \mathbf{E} + \mathbf{W} \tag{1}$$

where R is the rate of conversion of rock to weathered material,

D is the total denudation flux, E is the flux of weathered material removed by physical erosion, and W is the chemical weathering flux (all in mass per area per time). Each of the terms in Eqn. 1 is a mass flux; therefore the densities of rock and soil do not explicitly appear, nor are they necessary for the analysis that follows. Denudation rates are often reported in the literature in units of length per time, reflecting rates of land-scape lowering. These can be straightforwardly scaled by parent material density to yield the denudation mass flux used in our analysis. Note also that the cosmogenic nuclide literature often refers to total denudation rates (e.g., Kirchner et al., 1997). Here we use the term "physical erosion" to distinguish it as the physical component of the total denudation flux.

Conservation-of-mass equations like Eqn. 1 can also be written for individual elements of the rock and soil:

$$\mathbf{D} \cdot [\mathbf{X}]_{\text{rock}} = \mathbf{E} \cdot [\mathbf{X}]_{\text{soil}} + \mathbf{W}_{\mathbf{X}}$$
(2)

where  $[X]_{rock}$  and  $[X]_{soil}$  are the concentrations in rock and soil of an element X, and  $W_X$  is its chemical weathering rate. For immobile elements,  $W_X$  is zero (Fig. 3B) and Eqn. 2 reduces to

$$\mathbf{D} \cdot [\mathbf{Z}\mathbf{r}]_{\text{rock}} = \mathbf{E} \cdot [\mathbf{Z}\mathbf{r}]_{\text{soil}} \tag{3}$$

where  $[Zr]_{rock}$  and  $[Zr]_{soil}$  are the concentrations in rock and soil of an immobile element, in this case zirconium. Substituting Eqn. 3 into Eqn. 1 yields

$$W = D\left(1 - \frac{[Zr]_{rock}}{[Zr]_{soil}}\right)$$
(4)

Eqn. 4 expresses chemical weathering rate as a fraction of the total denudation rate, hereafter referred to as the "chemical depletion fraction" and denoted as CDF. The chemical depletion fraction,  $(1 - [Zr]_{rock}/[Zr]_{soil})$ , is the fraction of total denudation that is accounted for by chemical weathering.

The bulk chemical weathering rate of Eqn. 4 can also be partitioned into the weathering rates of individual elements. Substituting Eqn. 3 into Eqn. 2 directly yields,

$$W_{X} = D\left([X]_{rock} - [X]_{soil} \frac{[Zr]_{rock}}{[Zr]_{soil}}\right)$$
(5)

Note that the weathering rate  $W_X$  can be expressed in nondimensional form by normalizing by the total denudation rate for element X, as follows:

$$\frac{W_{X}}{D \cdot [X]_{rock}} = \left(1 - \frac{[X]_{soil}}{[X]_{rock}} \cdot \frac{[Zr]_{rock}}{[Zr]_{soil}}\right) = CDF_{X}$$
(6)

Normalized weathering rates from Eqn. 6 correspond to the negative of the mass transfer coefficient for weathering of element X in the approach of Brimhall et al. (1991, 1992; see also Brimhall and Dietrich, 1987; White et al., 1998; Anderson et al., 2002). They are similar to the chemical depletion fraction of Eqn. 4, except they express chemical weathering rates as a fraction of total denudation on an element-by-element basis, rather than for the soil as a whole. Hence we refer to them as "chemical depletion fractions of individual elements" (and denote them with  $CDF_x$ ).

### 3.3.2. Chemical weathering rates of saprolite

The mass balance approach of Eqns. 1 can be applied to individual soil units within a weathered profile, as well as to the regolith as a whole. For regolith composed of saprolite overlain by soil (as at Rio Icacos), if conversion of rock to saprolite is balanced by chemical weathering in the saprolite and physical conversion of saprolite to soil, then the mass of saprolite will be constant through time, such that

$$W_{\text{saprolite}} = D \left( 1 - \frac{[Zr]_{\text{rock}}}{[Zr]_{\text{saprolite}}} \right)$$
(7)

and

$$W_{X,saprolite} = D\left([X]_{rock} - [X]_{saprolite} \frac{[Zr]_{rock}}{[Zr]_{saprolite}}\right) \qquad (8)$$

where  $W_{saprolite}$  and  $W_{X}$ ,  $_{saprolite}$  are the chemical weathering rates for the saprolite as a whole and for an individual element X within it, respectively, and  $[Zr]_{saprolite}$  and  $[X]_{saprolite}$  are the concentrations of an immobile element (in this case zirconium) and element X in saprolite. Note that Eqn. 7 and 8 permit us to partition chemical weathering rates from the profile as a whole (obtained from Eqns. 4 and 5) into individual contributions from weathering of saprolite and soil, thus enabling quantitative study of chemical weathering patterns within regolith profiles.

#### 3.3.3. Volumetric strain

Using measurements of soil and rock density, together with weathering mass losses from immobile element enrichment, one can also calculate volumetric strain due to chemical weathering. Strain is the change in volume relative to the initial volume, so, for a volume of soil ( $V_{soil}$ ) created by chemical weathering from a volume of rock ( $V_{rock}$ ), strain ( $\epsilon$ ) can be expressed as

$$\varepsilon + 1 = \frac{V_{\text{soil}}}{V_{\text{rock}}} = \frac{(\rho_{\text{rock}} \cdot [Zr]_{\text{rock}})}{(\rho_{\text{soil}} \cdot [Zr]_{\text{soil}})}$$
(9)

Volumetric strain has been estimated in many studies of soil weathering and development (Brimhall and Dietrich, 1987; Brimhall et al., 1991, 1992; White et al., 1998; Anderson et al., 2002), but is not necessary for weathering rate calculations (e.g., Anderson et al., 2002; see also Eqns. 4 and 5), which are the focus of our work at Rio Icacos.

#### 3.3.4. Importance of parent material homogeneity

All soil mass balance methods, including ours, assume that immobile element enrichment reflects mass losses due to weathering. However, if soil is not generated from a single, uniform parent material, its weathering enrichment will be difficult to quantify, because its bulk chemistry will reflect mixing of multiple parent materials in addition to element depletion and enrichment due to weathering losses. For example, if a soil is generated from two rock types, there are two inputs in Eqn. 1 rather than one. Unless the relative rates of soil production from each rock type can be determined, their relative contributions to immobile element concentrations in the soil will be difficult to disentangle from the effects of weathering enrichment. Hence, mass balance methods like those in Eqns. 4 and 5 are best applied where soils are formed from a single parent material.

### 3.4. Quantifying Denudation Rates with Cosmogenic Nuclides

The geochemical mass balance of Eqns. 1–6 yields chemical weathering rates of soils and their component elements from measurements of immobile element enrichment, concentrations of constituent elements in rock and soil, and total denudation rates. Denudational mass flux rates (i.e., D of Eqns. 1 can be measured, over timescales comparable to those of soil formation, using cosmogenic nuclide methods. Because these methods have come into widespread use only in the past few years, the mass balance approach has only recently become applicable to eroding landscapes (Kirchner et al., 1997; Riebe et al., 2001).

<sup>10</sup>Be is produced in quartz grains near the earth's surface by cosmic ray neutrons and muons (e.g., Lal, 1991). Because quartz grains at depth are shielded from cosmic radiation, cosmogenic <sup>10</sup>Be concentrations in quartz grains reflect their near-surface residence times, and can be used to infer long-term average rates of outcrop erosion (Lal, 1991), landscape denudation (Brown et al., 1995; Bierman and Steig, 1996; Granger et al., 1996), and soil production (Heimsath et al., 1997; Small et al., 1999). Denudation rates from cosmogenic nuclides are averaged over roughly the timescale required to erode 160 g  $\cdot$  ${\rm cm}^{-2}$  of material, or ~60 cm for rock with density 2.6 g  $\cdot$  $\rm cm^{-3}.$  For a soil of density 1.3 g  $\cdot$   $\rm cm^{-3},~160~g$   $\cdot$   $\rm cm^{-2}$ corresponds to an equivalent soil thickness of  $\sim 120$  cm, which is often greater than soil depth in mountainous settings. Hence, in mountainous terrain, denudation rates from cosmogenic nuclides will typically be averaged over at least one soil residence time and are therefore well suited for quantifying soil formation rates. Detailed discussion on how cosmogenic nuclide measurements can be used to infer denudation rates (D) for use in Eqns. Eqns. 1-6 have been presented in previous work (e.g., Granger et al., 2001). Methods specific to this analysis are posted in the Electronic Annex (Elsevier website, Science Direct).

The surface production rate of <sup>10</sup>Be depends on sample latitude, because the cosmic ray flux depends on geomagnetic field strength and orientation (Lal, 1991). Due to secular variations in the geomagnetic field over the long timescales of cosmogenic nuclide accumulation in soils, the biggest source of uncertainty in denudation rates inferred in this analysis will be the <sup>10</sup>Be production rate, which is difficult to constrain because changes in the geomagnetic field are integrated over time as the sample is eroded from depth. However, uncertainty in the <sup>10</sup>Be production rate is unlikely to be more than 20% (Lal, 1991). Hence, long-term denudation rates from cosmogenic nuclides should have uncertainties of roughly 20%, as should most chemical weathering rates calculated from them using the geochemical mass balance of Eqns. 4 and 5.

The ability to measure long-term chemical weathering rates to within  $\pm 20\%$  would be unprecedented, particularly for measurements coupled with similarly precise estimates of longterm denudation rates. By applying the mass balance approach outlined above in a wide range of erosional and climatic settings, it should be possible to significantly advance our understanding of how chemical weathering, physical erosion and climate interrelate over long timescales (Riebe et al., 2001).

### 3.5. Sampling

For our weathering rate measurements at Rio Icacos, we chose small catchments spanning roughly 2 km along the watershed's western divide (Fig. 1), rather than focusing on a single small area. Our aim was to characterize any variability in chemical weathering rates across the site. Within each catchment we sampled soils, saprolite and rocks from widely distributed locations to characterize area-averaged bulk chemical compositions of unweathered quartz diorite and its weathered products; rather than focusing on a single small patch of soil, which could be anomalous, we averaged chemical weathering rates over broader, small-catchment scales.

# 3.5.1. Sampling soils, rock, and saprolite for bulk chemical analysis

Soils were sampled semirandomly. We divided our watersheds into grids with at least nine roughly equi-spaced points, and occupied the approximate grid point locations in the field. At each locality we dug pits (with depths up to 1 m) to sample the surface and basal soil horizons, or, if a tree throw with a soil-rich root wad happened to be nearby, we sampled the wad instead as an example of mixed material from depth. We also sampled material continuously along four deeper weathering profiles (2 each in catchments RI-4 and RI-7) using a hand auger (see Fig. 1 for locations). The auger profiles were up to 2 m deep and penetrated up to 1 m into saprolite. We also obtained saprolite samples from several landslide scars and from cutbanks along deeply incised reaches of the streams. Soil pits were located at high, mid, and low altitudes within each catchment, in an effort to sample weathered material from the widest possible range of conditions. Parent material was sampled from widely distributed outcrops within the catchments. We chose fresh outcrops wherever possible, but were occasionally limited to slightly altered material showing discoloration and staining (likely due to iron oxidation of mafic accessory minerals). Alteration was occasionally sufficient to induce a noticeable loss in grain-to-grain cohesion (compared to that of fresher rock), possibly due to biotite hydration, which causes expansive stresses that can shatter granite along grain-to-grain contacts (Larsen, 1948; Wahrhaftig, 1965). Two landslide scars within the catchments were deep enough that we could sample coherent, unweathered rock from basal exposures. In all we obtained 91 samples of soil, 32 samples of saprolite, and 24 samples of rock for analysis by X-ray fluorescence (details of our XRF procedures are included in the Electronic Appendix).

### 3.5.2. Sampling soils and sediment for cosmogenic nuclide analysis

The denudation rates in our weathering rate estimates from Eqns. 4 and 5 need to be spatially representative of our sampling areas, to ensure consistency with our weathering depletion estimates, which are averaged over catchment (10–20 ha) scales. Several studies (Brown et al., 1995; Bierman and Steig, 1996; Granger et al., 1996; Granger et al., 2001) have shown

that cosmogenic nuclide concentrations in well-mixed sediment can be used to infer the average denudation rate of the sediment's source area (even when different subareas within it are eroding at different rates), provided that denudation rates are fast enough that radioactive decay can be ignored. To apply this approach in our catchments, we sampled sediments from their streams for analysis of cosmogenic nuclide concentrations. We also sampled alluvial sediment pools on the trunk of Rio Icacos, at its gauge, and on Rio Sabana, a major tributary just west of our main sampling area, but still within quartz diorite bedrock (Fig. 1). We also collected samples from widely distributed soil surfaces in each of three different subareas of the catchments. Taking equal masses of these samples and amalgamating them for each subarea mimics the type of sediment mixing that we expect streams to accomplish naturally, assuming they mainly receive surface material. Hence we expect that cosmogenic nuclide concentrations in our amalgamated soil samples should be spatial averages that reflect the average denudation rates of the subareas.

### 4. RESULTS AND DISCUSSION

### 4.1. Element Concentrations, Chemical Depletion Fractions, and Element Mobility in Regolith

Table 1 lists average element concentrations from XRF analyses of Rio Icacos soils, saprolite, and rock for the catchments shown in Figure 1 (for results from individual samples see Table A1 in the Electronic Appendix). Chemical depletion fractions, calculated as  $(1 - [Zr]_{rock}/[Zr]_{soil})$  for each of catchments, indicate that chemical weathering accounts for between 58 and 68% of the total mass lost by denudation at Rio Icacos, assuming that Zr is immobile during chemical weathering (Table 2). Chemical depletion fractions can also be calculated from immobile elements other than Zr. However, Nb and Th, both thought to be highly immobile, are too scarce in rock and soil at Rio Icacos for reliable measurement by XRF. Y, another candidate, is highly depleted in saprolite and soil, relative to rock at Rio Icacos (Table 1), and is therefore unsuitable as an immobile element for tracing chemical weathering. Y depletion measured here is consistent with previous analyses of soils at this site (White et al., 1998).

The relative mobility of elements in saprolite and soil is illustrated by data from the hand-augered profiles in RI-4 and RI-7 (Fig. 1). Concentrations of Zr, Al, Ti, Fe, and Si, (Fig. 4A–E) are plotted against depth, revealing patterns of depletion and enrichment in the profiles. To facilitate comparisons among the profiles, which have different soil depths, we normalize depth by the depth to saprolite (i.e., with a depth = 1 being the depth of the soil-saprolite boundary). We also normalize element concentrations by their average concentrations in Rio Icacos rock, so that concentrations >1 (falling in shaded areas) correspond to relative enrichment, and concentrations <1 (falling in clear areas) correspond to relative depletion.

The profile data show that conversion of rock to saprolite entails significant mass losses of soluble elements, enriching Zr, Al, Ti and Fe (Fig. 4A–D) each by a factor of roughly 1.4. Hence Zr, Al, Ti and Fe all appear to be equally immobile in saprolite at Rio Icacos. Further weathering in soil enriches Zr to between 2.5 and 3.5 times its average concentration in rock (Fig. 4A). This translates to chemical depletion fractions of

Table 1. Average element concentrations (Rb, Sr, Y, and Zr, in ppm, all others in percent).

	Soil						
	RI-1	RI-2	RI-4	RI-7	Average		
Na	$0.12 \pm 0.01$	$0.10 \pm 0.01$	$0.15 \pm 0.04$	$0.15 \pm 0.02$	$0.13 \pm 0.01$		
Mg	$0.33 \pm 0.06$	$0.35 \pm 0.09$	$0.39 \pm 0.13$	$0.44 \pm 0.08$	$0.37 \pm 0.04$		
Al	$3.7 \pm 0.3$	$4.50 \pm 0.19$	$3.10 \pm 0.42$	$3.60 \pm 0.23$	$3.6 \pm 0.1$		
Si	$36.3 \pm 0.8$	$33.9 \pm 0.6$	$37.4 \pm 1.2$	$35.9 \pm 0.7$	$36.0 \pm 0.4$		
P	$0.009 \pm 0.001$	$0.013 \pm 0.001$	$0.011 \pm 0.001$	$0.012 \pm 0.001$	$0.011 \pm 0.001$		
K	$0.20 \pm 0.02$	$0.05 \pm 0.01$	$0.13 \pm 0.03$	$0.19 \pm 0.02$	$0.13 \pm 0.01$		
Ca	$0.32 \pm 0.08$	$0.37 \pm 0.10$	$0.44 \pm 0.16$	$0.50 \pm 0.09$	$0.41 \pm 0.04$		
Ti	$0.27 \pm 0.02$	$0.44 \pm 0.02$	$0.29 \pm 0.03$	$0.29 \pm 0.01$	$0.33 \pm 0.01$		
Mn	$0.045 \pm 0.007$	$0.049 \pm 0.007$	$0.049 \pm 0.012$	$0.053 \pm 0.007$	$0.050 \pm 0.003$		
Fe	$2.13 \pm 0.15$	$2.83 \pm 0.17$	$1.96 \pm 0.19$	$2.37 \pm 0.24$	$2.36 \pm 0.09$		
Rb	$11.5 \pm 1.6$	$4.8 \pm 0.2$	$8.0 \pm 1.1$	$10.7 \pm 0.9$	$8.0 \pm 0.5$		
Sr	$15.5 \pm 2.1$	$13.7 \pm 2.2$	$24.9 \pm 8.2$	$20.9 \pm 2.6$	$19.0 \pm 1.5$		
Y	$8.6 \pm 1.4$	$8.0 \pm 1.5$	$7.6 \pm 1.9$	$9.6 \pm 1.1$	$8.1 \pm 0.6$		
Zr	$205 \pm 10$	$264 \pm 14$	$234 \pm 15$	$230 \pm 12$	$236.9 \pm 5.8$		
n <sup>a</sup>	18	20	30	23	91		
			Saprolite				
	RI-1	RI-2	RI-4	RI-7	Average		
Na	0.08	$0.08 \pm 0.02$	$0.10 \pm 0.04$	$0.20 \pm 0.05$	$0.15 \pm 0.03$		
Mg	0.63	$0.54 \pm 0.42$	$0.63 \pm 0.13$	$0.82 \pm 0.17$	$0.72 \pm 0.10$		
Al	6.6	$6.30 \pm 0.08$	$6.50 \pm 0.07$	$6.30 \pm 0.14$	$6.4 \pm 0.1$		
Si	28.1	$29.8 \pm 0.4$	$29.1 \pm 0.1$	$29.0 \pm 0.3$	$29.1 \pm 0.2$		
P	0.013	$0.016 \pm 0.002$	$0.013 \pm 0.001$	$0.023 \pm 0.002$	$0.018 \pm 0.001$		
К	0.24	$0.18 \pm 0.15$	$0.27 \pm 0.02$	$0.29 \pm 0.04$	$0.27 \pm 0.02$		
Ca	0.22	$0.26 \pm 0.21$	$0.22 \pm 0.17$	$0.70 \pm 0.21$	$0.46 \pm 0.13$		
Ti	0.39	$0.42 \pm 0.01$	$0.43 \pm 0.01$	$0.41 \pm 0.01$	$0.42 \pm 0.01$		
Mn	0.051	$0.106 \pm 0.045$	$0.148 \pm 0.021$	$0.136 \pm 0.020$	$0.14 \pm 0.01$		
Fe	4.23	$3.35 \pm 0.11$	$3.42 \pm 0.05$	$3.35 \pm 0.08$	$3.40 \pm 0.05$		
Rb	17.7	$29.5 \pm 25.4$	$32.5 \pm 2.2$	$36.5 \pm 4.1$	$33.8 \pm 2.6$		
Sr	9.1	$9.8 \pm 1.8$	$11.1 \pm 5.5$	$23.3 \pm 6.4$	$17.1 \pm 4.0$		
Y	8.2	$57.7 \pm 54.1$	$6.4 \pm 1.6$	$14.9 \pm 2.2$	$13.9 \pm 3.5$		
Zr	171	$134 \pm 11$	$115 \pm 2$	$129 \pm 3$	$124.6 \pm 2.8$		
n <sup>a</sup>	1	2	13	16	32		
	Rock						
Element	RI-1	RI-2	RI-4	RI-7	Average		
Na	$1.26 \pm 0.02$	$1.29 \pm 0.04$	$1.28 \pm 0.01$	$1.20 \pm 0.03$	$1.26 \pm 0.02$		
Mg	$1.39 \pm 0.19$	$1.62 \pm 0.09$	$1.50 \pm 0.10$	$1.35 \pm 0.04$	$1.46 \pm 0.06$		
Al	$4.60 \pm 0.14$	$4.90 \pm 0.12$	$4.50 \pm 0.05$	$4.40 \pm 0.03$	$4.6 \pm 0.1$		
Si	$29.4 \pm 0.7$	$27.4 \pm 0.6$	$29.1 \pm 0.3$	$29.8 \pm 0.2$	$28.9 \pm 0.3$		
Р	$0.022 \pm 0.001$	$0.03 \pm 0.001$	$0.034 \pm 0.003$	$0.021 \pm 0.002$	$0.026 \pm 0.001$		
K	$0.53\pm0.02$	$0.32 \pm 0.02$	$0.39 \pm 0.02$	$0.54 \pm 0.03$	$0.45\pm0.02$		
Ca	$4.21\pm0.06$	$5.54 \pm 0.20$	$4.74 \pm 0.15$	$4.11 \pm 0.14$	$4.62\pm0.14$		
Ti	$0.27\pm0.02$	$0.35 \pm 0.02$	$0.28\pm0.01$	$0.28 \pm 0.01$	$0.30 \pm 0.01$		
Mn	$0.125 \pm 0.020$	$0.123 \pm 0.003$	$0.124 \pm 0.002$	$0.107 \pm 0.003$	$0.12 \pm 0.01$		
Fe	$2.17\pm0.24$	$2.59 \pm 0.12$	$2.24 \pm 0.06$	$2.20 \pm 0.12$	$2.30\pm0.08$		
Rb	$31.9 \pm 1.8$	$18.4 \pm 1.5$	$22.9 \pm 0.9$	$32.6 \pm 2.3$	$26.9 \pm 1.5$		
Sr	$216.2 \pm 10.7$	$304.4 \pm 11.4$	$316.5 \pm 22.8$	$204.6 \pm 7.0$	$255.7 \pm 12.1$		
Y	$23.7 \pm 4.5$	$24.4 \pm 1.2$	$18.8 \pm 0.8$	$19.8 \pm 0.5$	$21.7 \pm 1.2$		
Zr	$85 \pm 9$	$85 \pm 11$	$90 \pm 2$	$97 \pm 3$	$89.6 \pm 3.7$		
n <sup>a</sup>	6	6	5	7	24		

an = number of samples.

60–70%, roughly equal to the range of values that we infer for our catchments (Table 2). Conversely, Al, Ti, and Fe all show depletion in soil relative to saprolite (Fig. 4B–D), indicating that they are mobilized by chemical weathering after saprolite is converted to soil. Si (Fig. 4E) is more mobile than Zr, Al, Ti, and Fe (Fig. 4B–D) in saprolite, showing neither enrichment nor depletion relative to its average concentration in rock. After saprolite is converted to soil, Si becomes enriched by a factor of up to 1.3, but is nevertheless much more mobile than Zr, which doubles in concentration over the same interval.

Mobility relative to Zr in the profiles is more clearly revealed when concentrations are normalized by Zr enrichment, in ad-

Sample ID	Average elevation m	Average hillslope gradient m·m <sup>-1</sup>	Chemical depletion fraction <sup>a</sup> %	$10^{10} \text{Be}^{\text{b}}$ $10^{5} \text{ at g}^{-1}$	Apparent denudation rate <sup>c</sup> t•km <sup>-2</sup> •yr <sup>-1</sup>	Fraction of sample >2 mm %	Chemical weathering rate t•km <sup>-2</sup> •yr <sup>-1</sup>
Amalgamate	d soil samples						
RIS1 <sup>d</sup>	700	0.48	$59 \pm 5$	$2.06 \pm 0.11$	$79 \pm 18$	0	$47 \pm 11$
RIS2 <sup>d</sup>	700	0.48	$59 \pm 5$	$1.60 \pm 0.09$	$101 \pm 23$	11	$59 \pm 14$
RIS3 <sup>d</sup>	750	0.57	$61 \pm 2$	$1.76\pm0.10$	$97 \pm 22$	0	59 ± 13
Average soil	l samples						
RIS1, S2, ar	nd S3		$62 \pm 2^{e}$		$90 \pm 21^{\mathrm{f}}$		56 ± 13
Catchments	(with <sup>10</sup> Be measur	red from stream see	diment samples)				
RI-1	700	0.48	59 ± 5	$1.29 \pm 0.08$	$126 \pm 29^{g}$	24	N.A. <sup>g</sup>
RI-2	650	0.67	$68 \pm 5$	$0.96 \pm 0.07$	$184 \pm 46^{g}$	10	N.A. <sup>g</sup>
RI-4	750	0.57	$61 \pm 2$	$0.41 \pm 0.03$	$424 \pm 94^{g}$	70	N.A. <sup>g</sup>
RI-6	700	0.59	$62 \pm 2^{e}$	$1.08 \pm 0.06$	157 ± 35 <sup>g</sup>	13	N.A. <sup>g</sup>
RI-7	700	0.62	$58 \pm 3$	$1.22 \pm 0.09$	$135 \pm 31^{g}$	4	N.A. <sup>g</sup>
RI-8	650	0.59	$62 \pm 2^{\rm e}$	$0.66\pm0.04$	$247 \pm 55^{\mathrm{g}}$	55	N.A. <sup>g</sup>

Table 2. Chemical depletion fractions, apparent denudation rates and chemical weathering rates.

<sup>a</sup>Calculated from 1-[Zr]<sub>rock</sub>/[Zr]<sub>soil</sub> (using data from Table 1). Uncertainty is standard error.

<sup>b10</sup>Be calculated from <sup>10</sup>Be/<sup>9</sup>Be measured by Accelerator Mass Spectrometry at LLNL, and standardized against ICN <sup>10</sup>Be prepared by K. Nishiizumi (personal communication). See Electronic Appendix for analytical procedures. Uncertainty is standard error.

 $^{\circ}$ Soil depth = 95 ± 30 cm (average from profiles), soil density =  $0.9 \text{ g/cm}^3$  (from White et al., 1998). Production rates and penetration lengths for spallogenic production are corrected for geometric and depth shielding (Masarik et al., 2000). See Electronic Appendix for methods used to infer denudation rates from  $^{10}$ Be concentrations. Uncertainty is standard error and includes propagated effects of 20% systematic uncertainty in spallogenic  $^{10}$ Be production rates.

<sup>d</sup>RIS1 and RIS2 are from within catchment RI-1, and RIS3 is from within catchment RI-4.

<sup>e</sup>Site-wide averages of [Zr] in rock and soil used for chemical depletion fractions of the average soil and the large catchments RI-6 and RI-8. <sup>f</sup>Denudation rate of average soil is inverse-variance-weighted average of RIS1, RIS2 and RIS3.

<sup>g</sup>Our analysis suggests that cosmogenic nuclide concentrations in stream sediment do not reliably reflect catchment-wide denudation rates, due to effects of deep landsliding (see text). Hence, weathering rates, which are calculated in part from denudation rates (using Eq. 4), were not determined for the catchments.

dition to their average concentrations in rock, as shown in Figure 5 for Al, Ti, Fe, Si, Na, and Ca. In Figure 5, decreasing values below 1 reflect increasing mobility relative to Zr.

Assuming that Zr is immobile, its enrichment depends on (and thus is a direct reflection of) how much mass is lost by chemical weathering of the rock as a whole. Thus, by referencing an element's concentrations to Zr enrichment (as in Fig. 5), one can quantify how much of the element remains after chemical weathering, as a fraction of its original mass in the rock. In Figure 5, a value of 0 indicates all of the element's mass in the rock has been lost to weathering, whereas a value of 1 indicates the element has been enriched as much as Zr, and has therefore been immobile. For aluminum, titanium, and iron (Fig. 5A–C), data center around 1 in saprolite because they are immobile there, with enrichment roughly equal to that of Zr, as indicated in Figure 4. Figure 5D shows that Si is lost throughout the profile, with 25% being weathered away by the time saprolite is converted to soil, followed by an additional loss of 25% in the soil.



Fig. 4. Concentration versus depth (normalized to the depth of soil-saprolite boundary) for 4 hand-augered profiles, each with its own plot symbol (see Fig. 1 for locations), for Zr (A), Al (B), Ti (C), Fe (D), and Si (E), all normalized to their average concentrations in Rio Icacos rock. Shaded and clear areas correspond to relative enrichment and depletion, respectively. Zr, Al, Ti and Fe are all enriched by roughly the same amount in saprolite, suggesting they are equally immobile there, but of those four, only Zr shows continued enrichment above the saprolite, suggesting the others are depleted in soils. Si shows neither enrichment nor depletion in saprolite but is slightly enriched in soil.



Fig. 5. Concentration versus depth (normalized to the depth of soil-saprolite boundary) for the profiles of Figure 4, here normalized to both the average concentration in Rio Icacos rock, and also to the enrichment of Zr for Al (A), Ti, (B), Fe (C), Si (D), Ca (E), and Na (F). Assuming that Zr is immobile, a value of 0 indicates all of the element's mass in the rock has been lost to weathering, whereas a value of 1 indicates the element has been immobile. For Al, Ti, and Fe, data center around 1 in saprolite because they are immobile there, with enrichment roughly equal to that of Zr. Si is lost throughout the profile, with 25% being weathered away in saprolite, and an additional loss of 25% in the soil. Ca and Na are nearly absent in the saprolite indicating that weathering has mobilized most of the Ca and Na into solution.

Ca and Na are nearly absent in the saprolite (Fig. 5E,F), indicating that, below the depths sampled here, weathering mobilizes most of the Ca and Na into solution. This is consistent with bulk chemical and mineralogical data from (White et al., 1998), which demonstrate that most of the rock's Ca and Na are released into solution at the saprolite-rock boundary, when essentially all of the Ca and Na bearing minerals (i.e., plagioclase, K-feldspar and hornblende) are converted to kaolinite (Fig. 2), after White et al., 1998). The relative enrichment of silica-rich quartz and depletion of aluminum-bearing kaolinite in soils (Fig. 2) is consistent with enrichment of Si and depletion of Al shown in Figure 4B,E over the same depth interval.

### 4.2. Cosmogenic Nuclide Measurements of Denudation Rates

Cosmogenic nuclide concentrations were measured by Accelerator Mass Spectrometry at Lawrence Livermore National Lab and are reported in Table 2 (for details on our analytical procedures, see the Electronic Appendix). Table 2 also includes the catchments' characteristics and their apparent denudation rates, which were inferred from <sup>10</sup>Be concentrations using equations in the Electronic Appendix.

Cosmogenic nuclides in the three amalgamated soil samples (RIS1, RIS2 and RIS3), which include material from widely distributed locations on catchment slopes, imply denudation rates ranging between 79 and 101 (average = 90 ± 21) t · km<sup>-2</sup> · yr<sup>-1</sup>, in good agreement with previous cosmogenic nuclide work, which yielded a denudation rate of 68 t · km<sup>-2</sup> · yr<sup>-1</sup> from soil surfaces along the Guaba ridge (after Brown et al., 1995, assuming  $\rho_{\rm rock} = 2.7 \text{ g} \cdot \text{cm}^{-3}$ ). Agreement this close (to within a factor of 1.5) for four different areas (two in catchment RI-1, one in RI-4, and one from independent work nearby), suggests that denudation rates are roughly uniform across the site. Yet, by contrast, cosmogenic nuclides in stream sediment (RI-1, RI-2, RI-4, RI-6, RI-7 and RI-8 in Table 2) yield apparent denudation rates that vary by more than three-

fold across the site and are everywhere significantly higher than those inferred from the amalgamated soils (with a maximum of  $424 \pm 94 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$  in RI-4, where the soil sample RIS3 implies a denudation rate of only 97  $\pm 22 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$ ). Such discrepancies are inconsistent with the absence of obvious knickpoints and low-relief surfaces, which would be indicative of nonuniform rates of stream incision and hillslope evolution (e.g., Riebe et al., 2000). However, at Rio Icacos, landsliding is an important erosional process (e.g., Brown et al., 1995; Larsen, 1997), and may help to explain why cosmogenic nuclide concentrations in stream sediment imply catchment denudation rates that are up to 4–5 times higher than those of the amalgamated soil samples. We considered two different landslide-related interpretations of our cosmogenic nuclide data at Rio Icacos.

One interpretation is that the prevalence of landsliding (Larsen, 1997) and the variability in apparent denudation rates (Table 2) together imply that different areas have different long-term denudation rates, due to chronic differences in the number and extent of landslides-which are presumably more effective erosive agents than other processes, such as slope wash, tree throw and soil creep. However, there is no reason to expect that this should be the case, given that all of the factors that seem to control the distribution of landsliding at Rio Icacos (including aspect, precipitation, lithology, size, and average hillslope gradients; after Larsen and Torres-Sanchez, 1998) are similar among our catchments (see Fig. 1, Table 1, and Table 2 for comparisons). Hence there is no obvious mechanism for variability in the importance of landsliding over the long term, suggesting that the threefold variability in apparent denudation rates across our catchments (Table 2) is probably due to some other effect.

An alternative interpretation is that denudation rates inferred from cosmogenic nuclides in stream sediment may be both artifactually high and spuriously variable, because one or more of the assumptions of the cosmogenic approach may be invalid at landslide-prone Rio Icacos. One assumption of the approach is that individual areas within the catchment are eroding steadily, and with minimal episodicity, such that the depths of erosion events are not too great. For typical landslide depths and recurrence intervals at Rio Icacos (2 m and 10<sup>4</sup> yr; after Larsen, 1991; Larsen and Torres-Sanchez, 1992; Larsen et al., 1993), Brown et al. (1995) determined that cosmogenic nuclide concentrations should, on average, robustly reflect long-term denudation rates, implying that episodic erosion by typical events would not invalidate the cosmogenic approach. However, in our catchments we observed several landslides of atypical depths, with some exceeding 5 m. Material from that deep has been shielded from cosmic radiation such that <sup>10</sup>Be concentrations should be negligible in its quartz, effectively reflecting infinite denudation rates, if landslide depth were not taken into account in the analysis. Hence for catchments that include deep landslides, the average 10Be concentration in stream sediment will depend at least partly on how much of its quartz was introduced from great depth by landsliding, regardless of the contributing area's average denudation rate.

In catchments where deep landslides are not a concern, the cosmogenic nuclide approach should yield catchment-averaged denudation rates, if individual subareas within the catchment contribute sediment to streams in proportion to their long-term average denudation rates. If one subarea instead contributes a greater fraction, then the average nuclide concentration in stream sediment would be biased toward the cosmogenic nuclide concentration of the anomalous area, leading to a biased estimate of average denudation rate. At Rio Icacos sediment delivery rates from landslide scars depend on scar age, with higher than average rates after initial exposure, followed by slower than average rates as mosses and other vegetation become established (Larsen et al., 1999). Hence, the assumption that landslide areas contribute in proportion to their long-term denudation rates may often be invalid at Rio Icacos. Given that landslide scars have been shielded at depth from cosmic radiation, we would expect that average nuclide concentrations in stream sediments may often be biased toward lower, scarlike values, and that average scar age would be a dominant control on apparent denudation rates at Rio Icacos (with higher apparent rates for lower average scar ages). Landslide material will also be over-represented in streambed sediment if it is coarser than the average material eroded from the catchment, because the finer size fractions would be more readily winnowed from the streambed by the flow, preferentially leaving the coarser landslide-derived material behind. Hence the variability in cosmogenic nuclide concentrations in stream sediment shown in Table 2 could be due to either the mere presence of deep (>5m)landslides, or disproportionate sediment delivery from landslide scars.

This is borne out by previous cosmogenic analyses of Rio Icacos stream sediments, which show that <sup>10</sup>Be in stream quartz correlates strongly with sediment grain size (Brown et al., 1995, 1998), both at the river's trunk (near our sample RI-6, at the gauge) and also in the tributary Quebrada Guaba (just downstream of our samples RI-1 and RI-7). Finer quartz fractions have higher <sup>10</sup>Be concentrations, similar to those of soil surfaces that have not been subjected to recent landsliding, whereas coarser quartz fractions have lower <sup>10</sup>Be concentrations, similar to those in material from deep landslides (Brown et al., 1995, 1998). The coarser quartz in streams is apparently at least partly derived from deep saprolite, which is relatively poor in cosmogenic nuclides (due to shielding), and also yields relatively coarse sediment, because weathering has not had a chance to completely disaggregate it into finer fragments.

Hence, the coarser sediment samples at Rio Icacos have lower <sup>10</sup>Be concentrations, not necessarily because their contributing areas have higher denudation rates, but instead because their coarse fractions are derived, in part, from deep landslides. Our results are consistent with this hypothesis, indicating that <sup>10</sup>Be concentrations are lower in samples that have proportionally more coarse (>2 mm) material (Table 2 and Fig. 6). This suggests that the variability in <sup>10</sup>Be in stream sediment from catchment to catchment may be due to variability in contributions from deep landslides. Landslides deep enough to mine <sup>10</sup>Be-poor saprolite are present in all of our catchments; it seems likely that they have affected our stream sediment samples, given that the amalgamated soil samples (which are unaffected by landsliding) imply denudation rates that are all lower than what we infer from the stream sediments.

Hence we suggest that due to the effects of deep landslides, streams at Rio Icacos are unlikely to yield sediment with average cosmogenic nuclide concentrations that correspond to average denudation rates of their contributing areas. In contrast,



Fig. 6. <sup>10</sup>Be concentrations plotted against proportion of sample with grain size >2 for amalgamated soils (circles) and stream sediments (diamonds). Gray band is range of concentrations from landslide-derived material (taken from Brown et al., 1998). Amalgamated soil samples, which are unaffected by landsliding, have nuclide concentrations that are much higher than those of landslide-derived materials. <sup>10</sup>Be concentrations decrease with increasing fractions of coarse material for the stream sediments, suggesting that they are derived, at least in part, from deep landslides.

cosmogenic nuclides in the amalgamated soils, which include material from widely distributed locations on catchment slopes, should yield robust spatial averages of hillslope denudation rates that can be used in Eqns. 4, 5, 7, and 8 to estimate long-term chemical weathering rates.

## 4.3. Comparison of Short- and Long-Term Chemical Weathering Rates

Although rocks and soils from RI-2 have slightly less Si and correspondingly more Fe, Mg, and Ca compared to RI-1, RI-4, and RI-7 (see Table 1), element concentrations are generally consistent from catchment to catchment across the study area, suggesting that site-wide averages of them (Table 1) should be broadly representative of parent materials and the soils and saprolite that are generated from them by chemical weathering at Rio Icacos. Using the site-wide average element concentrations of Table 1 together with the long-term average denudation rate based on the amalgamated soil samples (90  $\pm$  21 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup>, from Table 2), we calculated long-term chemical weathering rates for each of the major elements, both as fluxes from saprolite alone (after Eqn. 8) and from the saprolite and soil as a whole (after Eqn. 5). Results are reported in Table 3. Losses in saprolite account for nearly 100% of both Na and Ca weathering (1.0 and 3.9 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup>, respectively). This is not because Na and Ca are immobile in the soil, but instead because almost no Na or Ca survives to be weathered above the saprolite-soil boundary (see Table 1). Roughly 50% of all Si weathering occurs in saprolite, whereas Al, Ti and Fe are immobile there (with weathering rates = 0, within estimated uncertainties).

Table 4 presents the long-term total chemical weathering

Table 3. Long-term chemical weathering rates from saprolite and soil (all in  $t \cdot km^{-2} \cdot yr^{-1})^a$ .

Element	Saprolite	Soil <sup>b</sup>	Total
	10 + 0.2	0.1 + 0.2	11 + 0.2
Na	$1.0 \pm 0.2$	$0.1 \pm 0.3$	$1.1 \pm 0.3$
Mg	$0.9 \pm 0.2$	$0.3 \pm 0.4$	$1.1 \pm 0.3$
Al	$0.0 \pm 0.2$	$2.9 \pm 0.7$	$2.9 \pm 0.7$
Si	$7.2 \pm 1.9$	$6.6 \pm 3.8$	$13.8 \pm 3.3$
Р	$0.012 \pm 0.003$	$0.008 \pm 0.006$	$0.020 \pm 0.005$
K	$0.23\pm0.06$	$0.13 \pm 0.11$	$0.37\pm0.09$
Ca	$3.9 \pm 0.9$	$0.2 \pm 1.3$	$4.0 \pm 0.9$
Ti	$0.00 \pm 0.02$	$0.16 \pm 0.04$	$0.15 \pm 0.04$
Mn	$0.02 \pm 0.01$	$0.07 \pm 0.02$	$0.09\pm0.02$
Fe	$-0.1 \pm 0.1$	$1.4 \pm 0.3$	$1.3 \pm 0.3$
Total as oxides <sup>c</sup> :	$25 \pm 7$	$31 \pm 15$	56 ± 13

<sup>a</sup>Uncertainty is standard error.

<sup>b</sup>Based on subtraction of saprolite contribution from total, with standard errors propagated by adding them in quadrature.

<sup>c</sup>Based on bulk chemical weathering rates inferred from Eqs. 4 and 7, for total and saprolite, and on subtraction of saprolite from total for soil.

Element	Long-term total saprolite+soil (this study)	Long-term total based on regolith profile (White et al., 1998) <sup>a</sup>	Short-term total based on pore waters (White et al., 1998) <sup>b</sup>	Short-term total based on solute fluxes (McDowell and Asbury, 1994) <sup>c</sup>
Na	$1.1 \pm 0.3$	1.4	3.1	2.5
Mg	$1.1 \pm 0.3$	0.8	1.6	2.8
Al	$2.9 \pm 0.7$	N.A.	N.A.	N.A.
Si	$13.8 \pm 3.3$	15.4	12.2	22.7
Р	$0.020 \pm 0.005$	N.A.	N.A.	N.A.
K	$0.37 \pm 0.09$	1.0	1.4	1.3
Ca	$4.0 \pm 0.9$	3.4	4.1	8.5
Ti	$0.15 \pm 0.04$	N.A.	N.A.	N.A.
Mn	$0.09 \pm 0.02$	N.A.	N.A.	N.A.
Fe	$1.3 \pm 0.3$	N.A.	N.A.	N.A.
sums:				
Na+Mg+Si+K+Ca:	$20.5\pm3.4$	22.0	22.5	37.7

Table 4. Comparison of short- and long-term chemical weathering rates (all in t·km<sup>-2</sup>·yr<sup>-1</sup>).

<sup>a</sup>Based on residence time and integrated mass losses of the regolith profile.

<sup>b</sup>Based on solute concentrations in pore waters and estimates of infiltration rates.

°Corrected for precipitation inputs by White and Blum (1995).

rates from Eqn. 5 along with three additional sets of chemical weathering rates measured from independent data in previous work at Rio Icacos. Comparisons among the data sets reveal that Ca and Si weathering rates and also the sum of Na, Mg, Si, K and Ca weathering from our work all agree with estimates from two of the other weathering data sets to within 1 standard error. None of the four sets of weathering rates in Table 4 is an unambiguous "gold standard" against which the others can be compared for verification of accuracy, because each employs assumptions that are difficult to validate. The agreement shown in Table 4 nevertheless suggests that, at Rio Icacos, our mass balance approach for measuring long-term chemical weathering rates from eroding soils is at least as accurate as the three other independent approaches.

Even so, differences in weathering rates of individual elements may be indicative of important limitations in one or more of the data sets. For example, according to Table 4, Na weathering rates over the short term are a factor of 2–3 higher than what the long-term rates would predict. The short-term rates are based on input-output mass balance calculations, so one way the discrepancy in Na weathering could arise would be if one or more of the input or output terms in the short-term rate calculations were erroneous. Given Rio Icacos' close proximity to the sea, it seems plausible that Na inputs from precipitation could have been underestimated in previous work. If so, then the Na fluxes implied by the short-term data would be artifactually high, and might be inconsistent with the long-term averages. Results in Table 4 suggest that this may be the case.

In the case of K weathering rates, our estimate is a factor of roughly 3-4 lower than not only the short-term rates, but the other long-term rate as well. Hence, potential errors in inputoutput terms of the short-term calculations alone cannot explain the discrepancy in estimated K weathering rates. One way such a discrepancy could arise would be if we underestimated the amount of K in parent material. This would occur if, for example, potassium-rich pegmatite, which we encountered but did not sample, contributed significantly to soil formation and weathering. Given that K comprises <1% of the Rio Icacos quartz diorite, pegmatite dikes underlying only a few percent of the area could substantially increase inventories of K for weathering and incorporation into soil. Hence we may have underestimated K weathering in this case. However, K weathering accounts for only  $\sim 3\%$  of all chemical weathering at this site, so any errors introduced by underestimating K weathering rates would have little effect on the estimate of the total.

If one data set stands out as being different from the rest, it is the short-term rates inferred from solute exports in stream water. Si, Mg and Ca fluxes from that set are all higher, by up to a factor of 2, than what the other three sets would suggest. In their analysis of denudation rates at Rio Icacos, Brown et al. (1995) have estimated that uncertainties in the weathering export data may be as high as  $\pm 50\%$ . Such large uncertainties could at least partly explain why that data set differs so much from the others. Another possible explanation is that recent landslides within the watershed have led to enhanced solute fluxes over the short term by exposing fresh, highly weatherable material. However, such an effect would be offset somewhat by the landslide-induced removal of material that has not yet weathered to the extent it would during normal exhumation through the profile by other, less episodic processes. Yet another possible explanation for the factor of 2 differences of Table 4 is that the solute exports, measured from stream water sampled near the Rio Icacos gauge, include significant weathering contributions from the eastern, volcanic ridge, which has a greater proportion of Ca-Mg silicates than the Rio Blanco quartz diorite. If so, then Ca, Mg, and Si weathering fluxes inferred from outputs at the gauge might all be high relative to what we and others (White et al., 1998) have estimated for the area, based on analyses from the relatively uniform quartz diorite of the western ridge. Data in Table 4 suggest that this may be the case.

We suggest that the agreement among the data sets shown in Table 4 confirms the accuracy of our mass balance approach, compared to a suite of more traditional techniques, and indicates that it can be widely applied for measuring long-term chemical weathering rates from eroding soils.

### 4.4. Steady-State Soil Depth

Eqn. 1 assumes that soil depth is in steady state. If this were not the case, then chemical weathering rates inferred from Eqns. 4 and 5 would be in error. Eqn. 1 would become

$$\mathbf{R} = \mathbf{E} + \mathbf{W} + \rho_{\text{soil}} \cdot d\mathbf{h}/dt \tag{10}$$

where dh/dt is the rate of change of soil depth h and  $\rho_{soil}$  is soil density. Hence, if the mass imbalance between soil production and total denudation is small compared to the weathering rate, the error will be small enough to ignore. Theoretical considerations and field observations suggest that this should be the case at Rio Icacos. If soil production rates decrease with increasing soil thickness, as theory has predicted (Gilbert, 1877; Dietrich et al., 1995) and as soil production measurements from hilly landscapes have shown (Heimsath et al., 1997), then soils should maintain relatively stable depths over the long term, even if soil production and removal become unbalanced from time to time (Dietrich et al., 1995). For example, if the rate of soil loss (i.e., by physical erosion and chemical weathering) decreases, soils will begin to thicken, causing soil production to decrease until it again balances soil removal, thus stabilizing soil depth at a slightly thicker value. If soil removal rates instead increased, soil depth would also stabilize, but at a slightly thinner value. Field observations suggest that soilforming processes at Rio Icacos are dominated by biogenic activity, which presumably decreases in effectiveness with increasing soil thickness. This implies that soil production rates probably vary inversely with depth, and that soil depth should therefore be roughly stable.

#### 4.5. Zirconium as an Immobile Element

Results from recent laboratory experiments suggest that Zr may not be completely impervious to chemical weathering (Hodson, 2002). However, field examples of Zr mobility are limited to lateritic soils (e.g., Hill et al., 2000), which are generally formed where chemical weathering rates are fast and physical erosion rates are slow, such that intensely altered soils are not quickly removed and replenished with fresh rock from below. Chemical weathering at Rio Icacos is intense enough to form etch pits on quartz (Schulz and White, 1999), which is highly insoluble. However, erosion rates are relatively fast compared to those of typical laterites, so exposure to intense weathering in soil (where Al, Ti and Fe are leached away; Figs. 4 and 5) will be relatively short. Using a range of typical soil thicknesses (0.5 to 1.5 m) and our estimates of average denudation rates (Tables 2 and 3) we can estimate approximate residence times for soils at Rio Icacos. Of the 90 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup> of total denudation at Rio Icacos (Table 2), 25 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup> is attributed to chemical weathering in saprolite (Table 3), and the remaining 65 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup> is accounted for by chemical weathering and physical erosion in the soil, implying residence times of only  $\sim$ 7–20 kyr, based on a soil density of 0.9 g  $\cdot$  $cm^{-3}$  measured by White et al. (1998). Hence, although we cannot rule out the possibility that some Zr is dissolved and lost from Rio Icacos soils, Zr dissolution significant enough to affect our analysis seems unlikely. Even in the unlikely case that 10% of the initial Zr has been dissolved away, the chemical depletion fraction, corrected for that loss, would be 65%, only

3% higher than what we infer assuming that Zr is immobile. Hence, our chemical weathering rates would be underestimated by less than 10%. Errors this small would not change any of the conclusions drawn from the comparisons in Table 4.

### 4.6. Eolian Fluxes

Our mass balance approach assumes that eolian fluxes have a negligible effect on soil bulk chemistry. This will be the case where eolian fluxes are small compared to total denudation rates. This should be true in mountainous Rio Icacos, where denudation rates of 79–101 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup> are much higher than any plausible inputs or outputs due to eolian processes. Soil formation continually supplies fresh material as physical erosion and chemical weathering remove altered products from catchment hillslopes. If eolian fluxes were large compared to rates of soil formation, we would observe evidence of eolian deposition and remobilization, but no such evidence is present at Rio Icacos.

# 4.7. Erosional and Climatic Effects on Chemical Weathering Rates

As indicated in Figures 4 and 5 and Table 3, measurable weathering of Al, Ti and Fe occurs in soil but not in saprolite. This is presumably because weathering is more aggressive in soils, compared to saprolite, as minerals are increasingly attacked by roots, organic acids and physical processes that shatter grains and increase mineral surface area. Enhanced chemical weathering of Al in soil, compared to saprolite, was also noted at Rio Icacos by White et al. (1998), who attributed it, in part, to the relative stability of kaolinite below the soil (Fig. 2), where biologic activity is demonstrably lower. This suggests that biologic agents may be important regulators of chemical weathering, and thus implies that climate should be an important regulator of chemical weathering rates as well. This is consistent with kinetic considerations (e.g., Lasaga, 1984), results from laboratory experiments (e.g., Brady and Carroll, 1994; White et al., 1999), and analyses of weathering rate data from around the world (e.g., Dunne, 1978; Drever and Zorbrist, 1992; Drever, 1994; White and Blum, 1995; Moulton and Berner, 1998), which suggest that weathering rates should depend on climatic factors such as runoff, altitude, vegetation, precipitation, and temperature.

However, mass balance results from our previous work at a series of temperate Sierra Nevada field sites (Riebe et al., 2001) imply that chemical weathering rates may also be highly sensitive to effects of differences in mineral supply rates from physical erosion of rock. Rates of denudation (Riebe et al., 2000) and chemical weathering (Riebe et al., 2001) vary by more than an order of magnitude across study catchments at two of our Sierra Nevada sites, Fort Sage and Fall River (Fig. 7). Moreover, weathering rates are strongly correlated with denudation rates, because chemical depletion is consistent from catchment to catchment (Fig. 7A), varying by only about twofold (Riebe et al., 2001). The strong correlation between rates of weathering and erosion (Fig. 7B) is not an artifact of the methods; although chemical weathering rates are calculated, in part, from denudation rates, there would be no strong relationship between them if faster-eroding soils were chemically



Fig. 7. Chemical depletion fractions and chemical weathering rates plotted against denudation rates for two Sierra Nevada, California, study sites where denudation rates vary substantially (after Riebe et al., 2001). Chemical depletion fractions (A) are relatively uniform from catchment to catchment at Fort Sage (open circles) and Fall River (closed circles), whereas chemical weathering rates (B) increase systematically with denudation rates. Lines correspond to relationships based on average chemical depletion fraction of 18%. Rates of chemical weathering and physical erosion appear to be tightly coupled across Fort Sage and Fall River, suggesting that chemical weathering rates may be supply-limited at these sites (see text).

fresher, with chemical depletion fractions varying inversely with physical erosion rates (indeed, that was our working hypothesis before we made our measurements). The strong coupling between rates of chemical weathering and denudation implies that chemical weathering rates may be significantly affected by site-to-site differences in the rate that fresh rock is incorporated into soils by physical erosion. This implies that any climatic effects on chemical weathering rates could be obscured by confounding mineral supply effects, if they are not accounted for or minimized.

For example, if denudation rates vary greatly from site to site, then climatic effects on chemical weathering rates might be difficult to disentangle from the effects of differences in erosion rates (and thus mineral supply). This appears to be the case even when results from temperate sites (like those of the Sierra Nevada) are compared alongside results from more extreme, tropical climates (like that of Rio Icacos). In Figure 8, long-term chemical weathering rates (from Eqn. 4) of Rio Icacos and the Sierra Nevada sites are plotted against mean annual temperature (Fig. 8A) and average annual precipitation (Fig. 8B) both as site-wide averages (closed circles) and for individual catchments (open circles). Although Rio Icacos posts the highest average chemical weathering rate (56  $\pm$  13 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup>; from Table 3) among these sites, the three rapidly eroding catchments from the much drier, cooler Fort Sage and Fall River sites (see also Fig. 7) have weathering rates of 60–110 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup>, roughly equal to and even exceeding the Rio Icacos weathering rates of 47–59 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup> (see Table 2). Equal or faster weathering rates in the three Sierra Nevada catchments are explained by their total denudation rates being three to eight times faster than Rio Icacos (293-680 versus 79–101 t  $\cdot$  km<sup>-2</sup>  $\cdot$  yr<sup>-1</sup>), while their chemical depletion fractions are only three to four times smaller (15-19% versus 58-68%). This is one reason why chemical weathering rates are not strongly correlated with either mean annual temperature or average annual precipitation across the wide range of climates sampled by our sites (Fig. 8A,B); any effects of climate on chemical weathering rates are at least partly obscured by the large variations in physical erosion rates among the catchments at individual sites.

Chemical weathering appears to be supply-limited at the Fort Sage and Fall River sites, with equal chemical depletion fractions across a wide range of denudation rates (Fig. 7). Weatherable minerals are apparently either rapidly consumed upon their incorporation into soils, or quickly rendered insoluble by coatings of relatively stable secondary minerals (e.g., Nugent et al., 1998). Supply-limited weathering would be consistent with the hypothesis that, for a given erosion rate, differences in chemical weathering rates should correspond to differences in climatic indices such as mean annual temperature and annual average precipitation. For example, in a hotter, wetter climate, more of the minerals in a given rock should be weatherable, so chemical depletion fractions, and thus chemical weathering rates, ought to be higher there for a given erosion rate. In that case, chemical depletion fractions, which are measures of weathering rates that are normalized by total denudation rates, should provide a rational framework for assessing the effects of climate on weathering, as shown in Figure 8C,D. When plotted against temperature and precipitation, chemical depletion fractions (Fig. 8C,D) show patterns that are more intuitively compelling than those shown by chemical weathering rates (Fig. 8A,B). For example, chemical depletion fractions appear to increase systematically with temperature, and are highest at Rio Icacos where precipitation is highest. We suggest that these patterns emerge because chemical depletion fractions effectively account for the catchment-to-catchment differences in erosion rates that obscure the effects of climate on chemical weathering rates themselves.

# 4.8. Mineral Supply Effects: The Importance of Differences in Bedrock Mineralogy

The strong erosional dependence of chemical weathering rates shown in Figure 7 suggests that chemical weathering rates may often be sensitive to the availability of fresh, weatherable



Fig. 8. Chemical weathering rates (A, B) and depletion fractions (C, D) plotted against mean annual temperature (A, C) and average annual precipitation (B, D) both for site wide averages (closed circles) and for individual catchments (open circles) from Rio Icacos (this study) and six drier, cooler sites from the Sierra Nevada Mountains, California (after Riebe et al., 2001). Chemical weathering rates are not strongly correlated with either mean annual temperature or average annual precipitation across our sites. Chemical depletion fractions, which are nondimensional measures of chemical weathering rates, appear to increase systematically with temperature, and are highest at Rio Icacos where precipitation is highest; apparently, chemical depletion fractions effectively account for the catchment-to-catchment differences in erosion rates that obscure the climatic effects on chemical weathering rates themselves.

surfaces from erosion. If so, then a rock's chemical weathering rate may depend on both its denudation rate and its weatherable mineral content, because the rate of supply of weatherable minerals to the soil should be equal to the product of the two. This implies that, in studies attempting to quantify climatic effects on chemical weathering rates, variability in bedrock mineralogy must be reduced as much as possible to minimize the potentially confounding effects of differences in mineral supply rates. Alternatively, mineralogical differences from site to site could possibly be accounted for by quantifying mineralspecific chemical weathering rates, according to mineral concentrations in rock and soil. Methods for such an analysis would closely follow the approach outlined for element-specific chemical weathering rates in Eqn. 5.

### 5. CONCLUSIONS

Our estimates of weathering rates of Si, Na, Ca, Mg, and K agree closely with three independent sets of weathering rate data, thus confirming the accuracy of our mass balance approach for measuring long-term chemical weathering rates. This approach can be used to measure chemical weathering rates in eroding landscapes with roughly uniform, crystalline bedrock, and therefore should be applicable in a wide variety of mountainous settings. Moreover, we suggest that our mass balance approach is a cost-effective alternative to traditional techniques for measuring chemical weathering rates. Our measurements from Rio Icacos required less than 4 weeks of field sampling and laboratory analysis; by comparison, conventional measurements of short-term weathering rates would require monitoring chemical fluxes in deposition and streamflow for years or decades. Furthermore, the mass balance approach is ideally suited for the study of geomorphic and soil-forming processes, because cosmogenic nuclide measurements average rates of chemical weathering and physical erosion over millennial timescales of mountain soil development (e.g., Nishiizumi et al., 1993; Bierman, 1994). Another attractive feature of the mass balance approach is that it can be applied at small scales (e.g., on soil surfaces, hillslopes and catchments), making it possible to choose sites that isolate specific factors of interest, to explore how and why weathering rates vary across landscapes.

Our analysis at Rio Icacos illustrates how the mass balance approach can be used to quantify weathering from individual units within regolith profiles, as well as from the soil as a whole. Physical erosion rates are also quantified as part of the mass balance approach, making it particularly useful for studying how rates of chemical weathering and physical erosion interrelate. Our results, coupled with previous analyses at a series of more temperate sites (Riebe et al., 2001), highlight the importance of nonclimatic, mineral supply effects in regulating chemical weathering rates. The rate of supply of weatherable minerals should be set by both the rate of physical erosion, which regulates how quickly fresh rock is incorporated into soil, and also the mineralogy of the rock itself.

Chemical depletion fractions measure chemical weathering rates as fractions of total denudation rates, and thus provide a measure of chemical weathering intensity. Unlike chemical weathering rates, chemical depletion fractions do not correlate with physical erosion rates (Riebe et al., 2001). Data from both Rio Icacos and the more temperate sites of our previous work (Riebe et al., 2001) indicate that chemical depletion fractions increase with increasing average temperature and precipitation, whereas any relationships between climate and chemical weathering rates are largely obscured by effects of site-to-site differences in mineral supply rates from erosion. Hence, climatic effects on chemical weathering rates clearly emerge across our sites only when chemical weathering rates are normalized by total denudation rates. Because rates of physical erosion and chemical weathering are measured together in our mass balance approach, it is well suited for analysis of such normalized weathering rates and can be used to determine, with unprecedented resolution, the relative importance of climatic and nonclimatic factors in regulating long-term chemical weathering rates.

Acknowledgments—We thank Chicory Bechtel for field assistance, Joe Troester (USGS WEBB program) and Fred Scatena (US Forest Service) for providing logistical support and access to the Luquillo Experimental Forest, Laura Glaser and Tim Teague for lab assistance, and Darryl Granger for instructive discussion on altitude scaling of muogenic <sup>10</sup>Be production. Thoughtful comments from Friedhelm von Blanckenburg, Ari Matmon and two anonymous reviewers improved the manuscript. This work was supported by NSF grant EAR-0000999 to Kirchner. Measurements of <sup>10</sup>Be were performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

Associate editor: R. Wieler

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