Rapid regolith formation over volcanic bedrock and implications for landscape evolution

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A B S T R A C T

The ability to quantify how fast weathering profiles develop is crucial to assessing soil resource depletion and quantifying how landscapes evolve over millennia. Uranium-series isotopes can be used to determine the age of the weathering front throughout a profile and to infer estimates of regolith production rates, because the abundance of U-series isotopes in a weathering profile is a function of chemical weathering and time. This technique is applied to a weathering profile in Puerto Rico developed over a volcaniclastic bedrock. U-series isotope compositions are modelled, revealing that it takes 40–60 kyr to develop an 18 m-thick profile. This is used to estimate an average regolith production rate of 334 ± 46 mm/kyr. This value is higher by a factor of up to 30 when compared to production rates estimated for weathering profiles developed over granitic or shale lithologies. This quantitatively underpins the lithological control on rates of regolith production (in a neighbouring watershed but over a granitic bedrock, production rates are only ~30–40 mm/kyr). Moreover, by comparing these results to a compilation of soil erosion rates, it is clear that landscapes are controlled by the balance (or imbalance) between regolith production and erosion: soil-mantled landscapes are the result of a relative balance between production and erosion, whereas in crateric areas, thicker weathering profiles are generated because erosion fails to match regolith production rates.

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1. Introduction

Quantifying the rate of conversion of bedrock into regolith through physical and chemical weathering is crucial for understanding landscape evolution over millennia and the coupling (or decoupling) between surface erosion at the top and bedrock weathering at the bottom of weathering profiles. The dynamics between these two interfaces dictate, at least partly, the evolution of soil resources, and more broadly of the Critical Zone (Brantley, 2008). Here we define regolith as the product of bedrock weathering as this term includes both the saprolite (the isovolumetric weathering product that retains the bedrock structure) and the overlying soil (the mobile uppermost layer of the weathering profile, produced from the saprolite by bioturbation, amongst other processes). In recent years, isotopic techniques have allowed us, for the first time, to quantify rates of regolith production. For instance, Heimsath et al. (1997) have used cosmogenic isotopes to show that soil production rates are inversely correlated to soil depth. To be able to discuss the evolution of soil resources, one needs to quantify soil erosion and production rates independently. However, the cosmogenic isotope technique requires assuming that these two rates are equal, suggesting that alternate approaches are needed to independently quantify rates of soil production. The measurement of uranium-series isotopes in erosion products can be used to determine the time elapsed since inception of bedrock weathering (Vigier et al., 2001, 2005, 2006; Dequincey et al., 2002; Dosseto et al., 2006a, 2006b, 2006c, 2008a, 2008b, 2010; Granet et al., 2007, 2010; Pelt et al., 2008; Ma et al., 2010). In a weathering profile, if one considers a sample at an elevation E, this timescale represents the amount of time elapsed between the time at which the bedrock–regolith interface was at elevation E and the present day (Fig. 1). Thus, this can be used to determine the age of the weathering front at different depths in a profile, termed throughout this manuscript the weathering age (Mathieu et al., 1995; Dequincey et al., 1999, 2002; Chabaux et al., 2003a, 2003b; Dosseto et al., 2008b; Pelt et al., 2008; Ma et al., 2010). Note that in previous studies this weathering age has been referred to as the soil or saprolite residence time. Regolith production rates can then be estimated either by considering the linear evolution of the weathering age with depth, when observed (as it

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is the case in this study), or by using the difference between the
elevation of the regolith sample considered and the current
elevation of the weathering front (Fig. 1). Note that neither
approach requires any assumption on the steady-state nature of the
profile thickness or knowledge of the denudation rate. This is illustrated in this
example where erosion is taken to be nil (the same concepts would apply to
actively eroding landscapes).

2. Study area

The studied weathering profile is located in the Bisley 1 catchment,
the first of a series of 5 adjacent research catchments that feed into the Mameyes river basin, in the Luquillo Mountains of
eastern Puerto Rico (Fig. 2). This basin drains north to the Atlantic Ocean and is underlain by marine-deposited basaltic to andesitic
volcaniclastic bedrock with a history of hydrothermal alteration related to the intrusion of the nearby quartz diorite stock. Relief in the
44 km² gaged area of the Mameyes watershed is characterized by steep slopes with elevation varying between 80 and
1050 m. Elevation in the Bisley watersheds ranges from 260 to
400 m. Mean annual temperature is 22 °C. Mean monthly tem-
peratures at the lowest elevations range from about 23.5 °C in
January to 27 °C in September, and from 17 °C to 20 °C at the highest elevations. Vegetation in the Mameyes watershed is
mostly subtropical to lower montane rainforest, with dwarf
forests at the highest elevations and Sierra Palm forests at lower
elevations. The Bisley catchments are mostly covered by Tabonuco Forest. Precipitation increases with elevation and ranges
from 3000 to 4000 mm yr⁻¹ (Scatena, 1990). The site was
logged extensively, but was reforested with native species
in the 1950s (Scatena, 1989).

Cores (approximately 10 cm diameter) were taken through a
weathering profile by hand-augering to 15.7 m depth at site B1R
(N18° 18.949, W65° 44.589), a 400 m elevation, ridge on the
divide between the Bisley 1 stream and a tributary of the Rio
Sabana (Fig. 2). The soils at the site are Ultisols of the Humatas
Series, which are 0.8–1.0 m deep, moderately well-drained, very-
fine, parasenesuic, isohyperthermic Typic Haplohumults (Scatena,
1989; Silver et al., 1994; NCRS, 2002). Beneath the soil is more
fine, parasesquic, isohyperthermic Typic Haplohumults (Scatena,
1989; Silver et al., 1994; NCRS, 2002). Beneath the soil is more
cosmogenic isotopes, respectively (Brown et al., 1995; Riebe
et al., 2003; Blaes et al., in revision). Thus, a comparison of these
two neighbouring catchments provides an opportunity to assess
the role of bedrock lithology, independent of climate, in control-
ing rates of soil production.

Fig. 1. Illustration of the concept of age of the weathering front, termed weather-
ing age, for two samples, A and B, in a profile. The weathering age for sample A,
A_{Awf,A}, represents the time elapsed between T₁, the time at which the bedrock-
regolith interface was at elevation E₂ and T_{now}, the present day: A_{Awf,A} = T_{now} - T₁. The
average regolith production rate over the distance E_{A,B}, where E₂ is the current
elevation of the bedrock-regolith interface, can be estimated simply as (E₂ - E₁)/
A_{Awf,A}. Alternatively, if the weathering age increases linearly with decreasing depth
(as it is the case in this study), the average regolith production rates over the
entire profile can be calculated from the slope of age as a function of depth. Note
that these approaches do not require any assumption on the steady-state nature of the
profile thickness or knowledge of the denudation rate. This is illustrated in this
example where erosion is taken to be nil (the same concepts would apply to
actively eroding landscapes).

Fig. 2. Simplified geological map of the Luquillo Critical Zone Observatory
showing locations of the Bisley (B1R) and Icacos (LG1; e.g. White et al., 1998)
weathering profiles in the Rio Mameyes and Rio Blanco catchments, respectively.
of the composition of the parent rock for comparison to the weathered samples. 11 out of 33 samples were analysed for U-series isotopes along with a bedrock sample. The scope of this article is restricted to discussing U-series isotope data, as mineralogical and other geochemical data will be discussed elsewhere.

3. Material and methods

Samples were homogenized and gently crushed in an agate mortar. About 30 mg of a solution enriched in $^{236}\text{U–}^{229}\text{Th}$ was added to $/C_{100}$ mg of sample. This was then dissolved in a mixture of HClO$_4$, HF and HNO$_3$. Fluorides were driven off by evaporation at 100 °C and samples were then dried down by step evaporation at 150 °C, 170 °C and 200 °C. They were then taken up in 7 M HNO$_3$ and loaded on a column containing AG1 × 8 anionic resin to separate U and Th. U and Th isotopes were measured on a Nu Instruments Nu Plasma multi-collector ICP–MS following procedures described in Sims et al. (2008). Accuracy was checked by analysing gravimetric standard BCR-2. Four replicate analysis yield a ($^{234}\text{U}/^{238}\text{U}$) activity ratio $\approx 0.991 \pm 0.006$ and ($^{230}\text{Th}/^{238}\text{U}$) $= 0.999 \pm 0.007$ (parentheses denote activity ratios throughout this article). Replicate analysis was performed for a sample and used to determine relative external analytical uncertainties. These values are poor for U and Th concentrations, respectively 7.7% and 6.4%, but as low as 0.2%, 0.03% and 1.2% for ($^{234}\text{U}/^{238}\text{U}$), ($^{230}\text{Th}/^{238}\text{U}$) and ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios, respectively. Poor external analytical uncertainty for U and Th concentrations could be explained by a heterogeneous distribution of these elements in the regolith. Note that this does not affect calculations and conclusions below, which are based on ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios only.

4. Results

The bedrock has U and Th concentrations of 0.75 and 1.04 ppm, respectively, which is generally lower than any values observed in the weathering profile (0.51–2.06 ppm and 1.43–2.67 ppm, respectively; Table 1). The ($^{234}\text{U}/^{238}\text{U}$) activity ratio in the bedrock is near secular equilibrium, whereas values greater than 1 are observed through the weathering profile (1.02–1.18). The ($^{230}\text{Th}/^{238}\text{U}$) in the bedrock is less than 1, and values in the weathering profile are all greater than 1 except for one sample (BIR370; sample depth $= 370$ cm). Except for sample BIR370, both ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) ratios increase with decreasing depth starting from near secular equilibrium at the bottom of the profile (Fig. 3). Note that there is evidence for sample BIR370 being less weathered compared to other samples: it has a CIA value of 89 (Table 1: Chemical Index of Alteration, CIA=(100)[Al$_2$O$_3$/Al$_2$O$_3$+CaO+Na$_2$O+K$_2$O]; Nesbitt and Young, 1982), compared to 97–99 in other samples (the weathering intensity increases with CIA values) (Supplementary Fig. 1);

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Depth (cm)</th>
<th>CIA</th>
<th>Th (ppm)</th>
<th>$2\sigma$</th>
<th>U (ppm)</th>
<th>$2\sigma$</th>
<th>($^{234}\text{U}/^{238}\text{U}$)</th>
<th>$2\sigma$</th>
<th>($^{230}\text{Th}/^{238}\text{U}$)</th>
<th>$2\sigma$</th>
<th>($^{230}\text{Th}/^{232}\text{Th}$)</th>
<th>$2\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>BIR4</td>
<td>4</td>
<td>96.7</td>
<td>2.292</td>
<td>0.003</td>
<td>1.184</td>
<td>0.001</td>
<td>1.165</td>
<td>0.002</td>
<td>1.340</td>
<td>0.004</td>
<td>2.097</td>
<td>0.003</td>
</tr>
<tr>
<td>BIR35</td>
<td>35</td>
<td>96.5</td>
<td>2.669</td>
<td>0.004</td>
<td>1.371</td>
<td>0.001</td>
<td>1.184</td>
<td>0.001</td>
<td>1.488</td>
<td>0.005</td>
<td>2.315</td>
<td>0.004</td>
</tr>
<tr>
<td>BIR132</td>
<td>132</td>
<td>96.5</td>
<td>1.686</td>
<td>0.001</td>
<td>1.888</td>
<td>0.003</td>
<td>1.135</td>
<td>0.002</td>
<td>1.365</td>
<td>0.005</td>
<td>4.628</td>
<td>0.009</td>
</tr>
<tr>
<td>BIR370</td>
<td>370</td>
<td>88.8</td>
<td>2.486</td>
<td>0.002</td>
<td>2.032</td>
<td>0.002</td>
<td>1.021</td>
<td>0.002</td>
<td>0.985</td>
<td>0.004</td>
<td>2.441</td>
<td>0.005</td>
</tr>
<tr>
<td>BIR587-1</td>
<td>687</td>
<td>95.4</td>
<td>1.561</td>
<td>0.002</td>
<td>0.552</td>
<td>0.000</td>
<td>1.092</td>
<td>0.002</td>
<td>1.250</td>
<td>0.006</td>
<td>1.335</td>
<td>0.004</td>
</tr>
<tr>
<td>BIR587-2</td>
<td>687</td>
<td>95.4</td>
<td>1.465</td>
<td>0.002</td>
<td>0.511</td>
<td>0.001</td>
<td>1.094</td>
<td>0.002</td>
<td>1.253</td>
<td>0.007</td>
<td>1.319</td>
<td>0.006</td>
</tr>
<tr>
<td>BIR841</td>
<td>841</td>
<td>98.2</td>
<td>1.437</td>
<td>0.002</td>
<td>0.802</td>
<td>0.001</td>
<td>1.068</td>
<td>0.001</td>
<td>1.187</td>
<td>0.006</td>
<td>2.005</td>
<td>0.007</td>
</tr>
<tr>
<td>BIR1012</td>
<td>1012</td>
<td>98.6</td>
<td>1.645</td>
<td>0.001</td>
<td>1.263</td>
<td>0.002</td>
<td>1.053</td>
<td>0.002</td>
<td>1.135</td>
<td>0.006</td>
<td>2.636</td>
<td>0.011</td>
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<tr>
<td>BIR1219</td>
<td>1219</td>
<td>98.4</td>
<td>2.091</td>
<td>0.002</td>
<td>2.065</td>
<td>0.003</td>
<td>1.048</td>
<td>0.001</td>
<td>1.125</td>
<td>0.005</td>
<td>3.365</td>
<td>0.010</td>
</tr>
<tr>
<td>BIR1433</td>
<td>1433</td>
<td>98.0</td>
<td>1.702</td>
<td>0.003</td>
<td>1.429</td>
<td>0.002</td>
<td>1.072</td>
<td>0.001</td>
<td>1.123</td>
<td>0.008</td>
<td>2.856</td>
<td>0.017</td>
</tr>
<tr>
<td>BIR1554</td>
<td>1554</td>
<td>96.5</td>
<td>1.426</td>
<td>0.001</td>
<td>1.798</td>
<td>0.002</td>
<td>1.062</td>
<td>0.002</td>
<td>1.070</td>
<td>0.004</td>
<td>4.091</td>
<td>0.010</td>
</tr>
<tr>
<td>Parent rock Bisley</td>
<td>n/a</td>
<td>67.9 ± 9.6</td>
<td>1.044</td>
<td>0.001</td>
<td>0.747</td>
<td>0.001</td>
<td>0.993</td>
<td>0.002</td>
<td>0.814</td>
<td>0.003</td>
<td>1.754</td>
<td>0.005</td>
</tr>
<tr>
<td>Rock standard BCR-2 (n = 4)</td>
<td>5.63</td>
<td>0.03</td>
<td>1.61</td>
<td>0.02</td>
<td>0.991</td>
<td>0.006</td>
<td>0.999</td>
<td>0.007</td>
<td>0.868</td>
<td>0.003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Errors for samples are internal analytical uncertainties given at the $2\sigma$ level. The error on the Chemical Index of Alteration (CIA) value of the parent rock is 1 standard deviation of 3 replicate analyses. Errors for the rock standard BCR-2 is $2 \times$ standard error determined from 4 replicate measurements.
it also has a WIP of 1390 (Weathering Index of Parker, WIP=(100)[(2Na₂O/0.35)+[MgO/0.9]+[2K₂O/0.25]+[CaO/0.7]]; Parker, 1970) compared to 224–498 in other samples (the weathering intensity increases with decreasing WIP values). Except for this sample, CIA values (97–99) are greater than those determined at a weathering profile developed over granodiorite in the neighbouring Rio Icacos catchment (92–95; values calculated from White et al., 1998). (230Th/232Th) ratios show large variations, between 1.32 and 4.63, and the bedrock has a (230Th/232Th) within this range with a value of 1.75. (230Th/232Th) ratios increase with depth in the saprolite. Unlike (234U/238U) and (230Th/238U) ratios, (230Th/232Th) can be controlled by the abundance of different mineral phases with variable U/Th ratios and, as explained below, the (230Th/232Th) ratio in the saprolite is likely controlled by the abundance of goethite (probably characterized by a high U/Th ratio, inducing an increase in (230Th/232Th) values where this mineral is abundant).

5. Discussion

5.1. U-series isotope behaviour in bedrock and regolith

Higher U and Th concentrations in the weathering profile compared to the bedrock indicate that during regolith development these elements are relatively immobile compared to major soluble elements such as Na or Ca (e.g. Brimhall and Dietrich, 1987). Although the absence of significant (234U–238U) disequilibrium in the bedrock would confirm that it has not undergone weathering, the presence of an excess of 238U compared to 234U (i.e. (230Th/238U) < 1) indicates either a recent loss of Th or a gain of U. This is surprising for two reasons: (i) if the rock is unweathered it should show secular equilibrium for this radioactive system too, especially considering that (230Th/238U) reaches equilibrium before 234U–238U; (ii) water–rock interaction generally solubilises U over Th, leaving the residue enriched in Th over U, which is opposite to what is observed here. Because the rock was collected from an outcrop, it is possible that it has undergone enough interaction with meteoric waters such that chemical weathering has disturbed the 230Th–238U equilibrium. Note that hydrothermal alteration cannot account for this disequilibrium as it took place more than 300 ka ago and any 238U–238U disequilibrium incurred would have decayed back to secular equilibrium. Interestingly, basaltic weathering rinds studied by Pelt et al. (2008) show similar (230Th/238U) ratios (0.76–0.92). Thus, it is possible that the bedrock sample is showing the early stages of weathering rind development with a (234U/238U) near unity and a (230Th/238U) less than 1 (as observed in the weathering rind the closest to the interface with the fresh bedrock in Pelt et al., 2008). Although not discussed in Pelt et al., the (230Th/238U) ratio less than 1 is compatible with the hypothesis of a gain of U, which they invoked to explain U/Zr and (234U/238U) ratios.

(234U–238U) radioactive disequilibrium in solids is observed as a result of (i) recoil of 234U into the surrounding medium (only measurable when the solid is fine-grained, typically silt size or smaller), (ii) preferential leaching of 234U located in damaged sites of the crystalline network (Kigoshi, 1971; Fleischer, 1980, 1982;ussin and Lal, 1986). Thus, the absence of 234U–238U disequilibrium in the bedrock sample, combined with the observation of 230Th–238U disequilibrium, could suggest that preferential leaching of 234U over 238U is not a significant process.

The continuous evolution of (234U/238U) and (230Th/238U) ratios in the weathering profile, diagnostic of increasingly weathered and older regolith material with decreasing depth, contrasts with the lack of systematic variation of weathering indexes such as CIA or WIP. The CIA is positively correlated with Fe(III)-oxides and kaolinite and inversely correlated with quartz, reflecting precipitation of secondary minerals and dissolution of quartz (Supplementary Table 1). Because the CIA and WIP parameters do not have an inherent time constraint (i.e., radioactive decay) and are affected by multiple geochemical and biogeochemical reactions, they are less robust proxies for weathering history than U-series isotopes. For instance, Price and Velbel (2003) tested the various indices of weathering commonly used by the community and concluded that CIA (along with other indices) is sensitive to other geochemical processes in addition to weathering (e.g., hydrothermal alteration and other forms of metamorphism). Moreover, an increase in CIA values with decreasing depth would be expected if CIA solely recorded weathering. However, CIA values in the top half of the profile are lower than in the bottom half. This could be explained by atmospheric input of Na, K and/or Ca, the precipitation of secondary phases or by differential hydrothermal alteration histories of the protolith of the upper and lower parts of the regolith profile.

U concentrations, U/Th and (230Th/232Th) ratios show a broad positive correlation with goethite abundance (Fig. 4). Noting that the lowest U concentration is in the bedrock, this suggests that the precipitation of goethite controls the abundance of uranium. Indeed, uranium is known to be strongly sorbed to hydrous ferric oxides, such as goethite, in oxic systems at near-neutral pH (e.g., Manceau et al., 1992; Moyes et al., 2000; Giammar and Hering, 2001) and sorption onto oxide and clay minerals has been shown to control uranium concentrations in soils (e.g., Gadelle et al., 2001). Moreover, this process seems to also control the (230Th/232Th) ratios in the regolith, where the range of observed values represents variable contributions between a “bedrock” end-member and a “goethite” end-member, the latter being characterized by a high (230Th/232Th) ratio. U concentrations and (230Th/238U) ratios are also positively correlated with P₂O₅ concentrations (not shown), suggesting that the formation of a phosphorus-bearing phase could also partially control these geochemical parameters or reflecting adsorption of phosphate onto goethite. In contrast, (234U/238U) and (230Th/238U) ratios show no correlation with goethite content or any of the minerals quantified.

5.2. Timescale of regolith development

As the weathering front progresses downward into the bedrock, the extent of weathering should increase with decreasing depth in the weathering profile, and the time elapsed since
production from the bedrock should increase with decreasing depth. Thus, since radioactive disequilibrium increases with time and extent of chemical weathering, an increase in disequilibrium with decreasing depth in the weathering profile is expected. Most previous work using U-series isotopes have focused on soils developed over granitic parent rock and this simple pattern of isotopic evolution was seldom observed (Mathieu et al., 1995; Dequincey et al., 1999, 2002, 2008b; Chabaux et al., 2003a, 2008). This is explained as weathering is not the only process occurring in soils but is accompanied by the complex transport of chemical elements and the precipitation and re-dissolution of secondary minerals. Nevertheless, here we observe that radioactive disequilibria for $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ increases with decreasing depth (Fig. 3), similarly to what has been recently observed for soils developed over shales (Ma et al., 2007). The question why soils derived from granitic rocks would have a more complex U–Th history than those developed on clastic rocks is puzzling and should deserve more attention. Although a discussion of the age of the weathering front, at different depths in the profile.

In this section, we use the U-series isotope composition of the regolith to model the time elapsed since onset of weathering, i.e. the age of the weathering front, at different depths in the profile.

In the model below, only $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ are considered for the following reasons (Tables 2 and 3): (i) unlike $(^{230}\text{Th}/^{232}\text{Th})$ or the Chemical Index of Alteration, $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ are not affected by bedrock composition heterogeneity (including hydrothermal alteration, which has occurred here). This is because as long as the rock has been in a closed system for more than 1 Ma prior to weathering (which is the case here) $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})=1$, regardless of composition heterogeneities. (ii) $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ are not affected by the selective dissolution of minerals. For instance, if we assume two minerals, A and B, with different U/Th ratios, where U/ThA > U/ThB. If mineral A is completely dissolved during weathering, this will result in a relative decrease of U/Th and $(^{230}\text{Th}/^{232}\text{Th})$ ratios of the bulk material. Thus, the variation in $(^{230}\text{Th}/^{232}\text{Th})$ has no time information and cannot be used in the model. This is not the case for $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$: if mineral A is completely dissolved, any disequilibrium that was created during dissolution of mineral A is entirely transferred to the solution and the bulk material will have the isotopic composition of the residual minerals. Thus, $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ ratios in the regolith are controlled by the isotopic composition of residual, U-bearing, actively dissolving minerals (e.g. micas, apatite if not completely dissolved; monazite is likely to be consumed early during weathering, whereas zircon are unlikely to dissolve in most cases). (iii) $(^{230}\text{Th}/^{232}\text{Th})$ correlates with goethite content suggesting that variations in this ratio are the

### Table 2
Criteria of selection of geochemical parameters (Chemical Index of Alteration (CIA) and U-series activity ratios) for the presented model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CIA</th>
<th>$(^{230}\text{Th}/^{232}\text{Th})$</th>
<th>$(^{234}\text{U}/^{238}\text{U})$</th>
<th>$(^{230}\text{Th}/^{238}\text{U})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitive to bedrock heterogeneity (incl. Hydrothermal processes)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Sensitive to the selective dissolution of minerals</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Correlates with goethite content</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Good index of weathering even in extensively weathered profiles</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Used in the model</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### Table 3
Results from the nuclide loss-gain model.

<table>
<thead>
<tr>
<th>Model</th>
<th>11 Samples solved. Initial conditions -- secular equilibrium</th>
<th>10 Samples solved. Initial conditions -- secular equilibrium</th>
<th>11 Samples solved. Initial conditions -- measured bedrock</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{238}$ (yr$^{-1}$)</td>
<td>$0.948 \pm 0.009 \times 10^{-5}$</td>
<td>$1.05 \pm 0.01 \times 10^{-5}$</td>
<td>$1.73 \pm 0.03 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_{234}/k_{238}$</td>
<td>$1.09 \pm 0.01$</td>
<td>$1.07 \pm 0.1$</td>
<td>$1.40 \pm 0.02$</td>
</tr>
<tr>
<td>$k_{230}$ (yr$^{-1}$)</td>
<td>$5.01 \pm 0.8 \times 10^{-18}$</td>
<td>$5.57 \pm 0.8 \times 10^{-18}$</td>
<td>$18 \pm 2 \times 10^{-18}$</td>
</tr>
<tr>
<td>$f_{234}f_{238}$ (yr$^{-1}$)</td>
<td>$0.93 \pm 0.02 \times 10^{-5}$</td>
<td>$1.16 \pm 0.04 \times 10^{-5}$</td>
<td>$0.40 \pm 0.01 \times 10^{-5}$</td>
</tr>
<tr>
<td>$f_{230}$ (yr$^{-1}$)</td>
<td>$1.58 \pm 0.02$</td>
<td>$1.57 \pm 0.02$</td>
<td>$3.10 \pm 0.06$</td>
</tr>
<tr>
<td>Weathering age (kyr)</td>
<td>$1.0 \pm 0.2 \times 10^{-5}$</td>
<td>$1.4 \pm 0.2 \times 10^{-5}$</td>
<td>$0.021 \pm 0.003 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Where 11 samples were solved, this included replicate analyses of sample BIR887. Where 10 samples were, we left out sample BIR170, which shows evidences of little weathering and probably represents a corestone (see text for details). All errors are 2 standard errors, except for the regolith production rate where the error reported is 1 standard error.
result of the variable abundance of this mineral phase, unrelated to the duration of weathering. \((^{234}\text{U}^{238}\text{U})\) and \((^{230}\text{Th}^{238}\text{U})\) do not show any correlation with secondary mineral contents. Hence, note that the timescale calculated with these two ratios is not that of goethite formation. (iv) For extensively weathered profiles as it is the case here, common indices of weathering (like CIA) are of little use because all soluble elements have been already mobilized. \((^{234}\text{U}^{238}\text{U})\) and \((^{230}\text{Th}^{238}\text{U})\) ratios do not have this limitation as they record weathering of residual mineral phases and U is less mobile than Ca, Mg, Na and K. Thus, these two isotopic ratios are valuable indices of weathering.

Dequincey et al. (2002) have proposed a model, later modified by Dosseto et al. (2008b), to describe the evolution of nuclide abundance with time in regolith material:

\[
\frac{dN_j}{dt} = \lambda_j N_i - \lambda_j N_j + f_j N_{i,0} - k_j N_j
\]

where \(\lambda_j\) is the decay constant of the parent nuclide, \(N_i\) the abundance of the parent nuclide in the sample, \(\lambda_j\) the decay constant of the nuclide, \(f_j\), an input coefficient for the nuclide \(j\) (in \(\text{yr}^{-1}\)), \(N_{i,0}\) the initial nuclide abundance and \(k_j\) a dissolution coefficient for the nuclide \(j\) (in \(\text{yr}^{-1}\)). The input and dissolution coefficients are the time constants at which nuclide addition via chemical illuviation and/or dust input and removal via chemical weathering occur, respectively. These coefficients represent the different rates at which nuclide gain and loss operate. Using this model, the \((^{234}\text{U}^{238}\text{U})\) and \((^{230}\text{Th}^{238}\text{U})\) ratios in a regolith sample at a given depth are a function of the gain and loss coefficients for \(^{238}\text{U}, ^{234}\text{U}\) and \(^{230}\text{Th}\), and the amount of time elapsed since onset of bedrock weathering, i.e. the age of the weathering front \(A_{\text{wbf}}\) at that depth (Fig. 1).

A major assumption of the model is that, although they take different values for each nuclide, they are assumed to be constant throughout the profile and over the age of the weathering front. A second major hypothesis is that nuclide gain (illuviation and/or dust input) occurs over a similar timescale to nuclide loss (chemical weathering). Although it is likely that these processes occur over different timescales, there are not enough constraints to allow nuclide loss and gain to operate over different timescales in the model presented. Another possible pitfall of the model is that the gain of nuclides does not differentiate between the precipitation of secondary mineral and dust input. Nevertheless, dust input in the saprolite must be minimal (because of the nature of the saprolite, dust cannot be mechanically mixed with it) and secondary mineral precipitation must dominate.

The age of the weathering front, \(A_{\text{wbf}}\), will be different for each regolith sample, where \(A_{\text{wbf}}\) is expected to increase with decreasing depth in the weathering profile. Thus, we look for the set of \(k\) and \(f\) coefficients for the weathering profile, and \(A_{\text{wbf}}\) values for each sample that best reproduce the observed compositions. Considering the eleven samples analysed (including the replicate measurement of sample BIR687 to assess the sensitivity of the model to analytical error) and two activity ratios for each sample, \((^{234}\text{U}^{238}\text{U})\) and \((^{230}\text{Th}^{238}\text{U})\), we have 22 input parameters and 17 output parameters, or unknowns. We use a large-scale trust-region-reflective algorithm provided with the Matlab\textsuperscript{TM} software to minimize the squared difference between calculated and observed activity ratios. This algorithm is a subspace-trust region method based on the interior-reflective Newton method described in Coleman and Li (1994, 1996). Because the solution could represent a local minimum, we generate a large population of solutions \((n > 100)\) from which the retained solution is the median of this population and the error on the calculated parameters (gain and loss coefficients and weathering ages) is the standard error of this population.

Results from the model are shown in Table 2. We considered different scenarios: model 1 uses the 11 samples measured and assumed secular equilibrium as initial conditions. Model 2 excludes BIR370 as it is considered as an outlier on many aspects. Model 3 considers all the 11 samples measured but uses the measured composition of the bedrock sample as initial conditions. Results show that firstly, whether we consider as initial conditions a bedrock in secular equilibrium (i.e. before any water-rock interaction occurred; model 1) or the composition of the measured bedrock sample (model 3) this does not seem to significantly affect calculated weathering ages. Secondly, the model yields similar ages for replicate measurements of sample BIR687 (for instance, 26.8 and 27.2 kyr in model 1). Thirdly, calculated ages increase with decreasing depth, confirming the “ageing” of the regolith upward in the weathering profile. Note that, when taking a weathering age equal to 0 for the bedrock, its \((^{234}\text{U}^{238}\text{U})\) ratio follows the correlation defined by soil samples, whereas its \((^{230}\text{Th}^{238}\text{U})\) falls below (Supplementary Fig. 2). In the latter case, this indicates that (i) either the unweathered bedrock shows an excess of U over Th and chemical weathering follows a \(1-e^{-\text{t}/\tau}\) law where U is rapidly mobilized during the early stages of weathering (\(\tau\) being a characteristic timescale for weathering). This is unlikely as the bedrock is older than 1 Myr and it should be in secular equilibrium for \(^{230}\text{Th}\)–\(^{238}\text{U}\); (ii) the bedrock is not representative of the unweathered bedrock composition and this indicates that the early stage of bedrock weathering is characterized by a loss of Th over U, or enrichment of U over Th. The latter hypothesis is supported by the observation of similar \((^{230}\text{Th}^{238}\text{U})\) ratios in our bedrock sample and in weathering rinds from a basaltic corestone (Pelt et al., 2008).

Results from our calculations suggest that 40–60 kyr have elapsed since the weathering front migrated from where the topsoil is today to its current position, i.e. a weathering age for the topsoil of 40–60 kyr (model 1, Fig. 5). Extrapolating the relationship between age and depth to 0 yr, the current position of the weathering front can be estimated at a depth of \(\sim 16\) m, very close to the maximum depth at which augering was possible. Moreover, the relative linear relationship between age and depth (ruling out sample BIR370) suggests that the migration rate of the weathering front has been relatively constant over the past 40–60 kyr. The regolith production rate, i.e. the migration rate of the weathering front, can be determined as the slope in a weathering
age versus depth space:

\[ R = \frac{\Delta D}{\Delta \text{Awf}} \]  

(2)

where \( R \) is the regolith production rate (in mm/kyr) and \( D \) is depth (in mm). The age of the weathering front, \( \text{Awf} \), is in thousands of years. In this case, the slope in Fig. 6 yields an average regolith production rate of \( 334 \pm 46 \text{ mm/kyr} \) (error is \( 2\sigma \)). This value is greater than any production rate that has been determined from U-series isotopes thus far (Fig. 7). Indeed, previous studies of weathering profiles developed over granitic or shale substratum have yielded values between 10 and 70 mm/kyr. Thus, our results could suggest that weathering profiles over volcaniclastic substratum are produced up to 30 times faster than in granitic regions. Note that this work is the first of its kind and further studies of volcaniclastic weathering profiles need to be undertaken before this statement can be generalized. Although it is well known that different lithologies weather at different rates, producing regolith more or less rapidly, we are now able to quantify these differences. The geomorphic settings of the production rates compiled in Fig. 8 vary: cratons in Brazil and Burkina-Faso (Mathieu et al., 1995; Dequincey et al., 2002), soil-mantled hillslopes in Australia and eastern US (Dosseto et al., 2008b; Ma et al., 2010) and a landslide-dominated landscape in Puerto Rico (this study and Dosseto et al., 2007). However, the range of production rate values is narrow compared to that of soil erosion rates reported in Montgomery (2007) (Fig. 8). Thus, results from U-series studies suggest that, in general the weathering profile thicknesses are in steady-state on soil-mantled hillslopes around the world (soil erosion–production) as proposed earlier using geomorphic transport laws (Fernandes and Dietrich, 1997) or cosmogenic isotopes (Heimsath et al., 1997) and previously verified using both U-series and cosmogenic isotopes at a site in southeastern Australia (Dosseto et al., 2008b). Nevertheless, regolith production seems faster than erosion on cratons, suggesting that weathering profiles in these regions are inexorably thickening. In comparison, regolith production is not matched by erosion in alpine environments (Fig. 8), possibly accounting for the bare rock landscape of these regions. However, studies need to be undertaken in tectonically active environments in order to test this hypothesis. Finally, it is clear that, even in the light of our results, natural rates of regolith production are too low compared to erosion rates in cultivated areas. The quantitative determination of regolith production rates using U-series isotopes allows us to estimate that regolith is lost 100–1000 times faster than it is renewed in regions impacted by human activity.

6. Conclusions

- A weathering profile developed over volcaniclastic bedrock under a tropical climate was studied with uranium-series isotopes to determine time constraints on soil formation in this environment.
- Bedrock collected from an outcrop show \( ^{230}\text{Th} - ^{238}\text{U} \) disequilibrium similar to that observed in weathering rinds, but with
$^{234}\text{U}}-^{238}\text{U}$ in equilibrium indicating that (i) very early stages of water-rock interaction differentially mobilize chemical elements such as Th and U, and (ii) preferential leaching of $^{234}\text{U}$ over $^{238}\text{U}$ is not a significant process, at least for this lithology.

- Common indexes of chemical weathering (CIA, WIP) do not show any systematic variation through the profile. This is explained as they do not record the weathering of primary minerals solely, but also the formation of secondary phases and pre-weathering metamorphic alteration (U-series being insensitive to the latter, having occurred more than 1 Ma ago).

In contrast, $^{238}\text{U}}-^{234}\text{U}-^{230}\text{Th}$ radioactive disequilibria systematize with decreasing depth, as expected from an increasingly weathered profile from bottom to top.

- Modelling of U-series isotope composition in regolith indicates that it takes 40–60 kyr to produce 18 m of weathering profile. The relationship between age of the weathering front and depth suggests that unweathered bedrock is located at ~16 m depth and that the rate of migration of the weathering front (i.e. the regolith production rate) has been relatively constant over the past 40–60 kyr.

- A regolith production rate of 334 ± 46 mm/kyr is calculated. This is greater than any previously calculated rates for granitic and shale lithologies by a factor of 5–30. Although further studies of volcaniclastic weathering profiles need to verify such fast production rates, these results appear to underline the role of lithology on regolith formation rates, here quantitatively demonstrated. In particular, production rates of 30–50 mm/kyr were determined for a weathering profile developed over quartz diorite in the neighbouring catchment of Rio Icacos, hence under similar climate (Blaes et al., in revision).

- A compilation of U-series regolith production rates show that steady-state weathering profile thickness is achieved in soil mantled landscapes. Nevertheless, in cratons, regolith production is faster than erosion and weathering profiles are thickening, whereas in cultivated areas, regolith is lost 100 to 1000 times faster than it is renewed.

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Appendix A. Supplementary material

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References


