UNIVERSITY
OF WOLLONGONG
AUSTRALIA

University of Wollongong
Research Online

Faculty of Science, Medicine and Health - Papers

Faculty of Science, Medicine and Health

2013

Soil formation rates determined from Uranium-series isotope disequilibria in soil profiles from the southeastern Australian highlands

P O. Suresh

Macquarie University, suresh.puthiyaveetil-othayoth@mq.edu.au

A Dosseto

University of Wollongong, tonyd@uow.edu.au

P P. Hesse

Macquarie University

H K. Handley

Macquarie University

Publication Details

Suresh, P. O., Dosseto, A., Hesse, P. P. & Handley, H. K. (2013). Soil formation rates determined from Uranium-series isotope disequilibria in soil profiles from the southeastern Australian highlands. *Earth and Planetary Science Letters*, 379 26-37.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library:
research-pubs@uow.edu.au

Soil formation rates determined from Uranium-series isotope disequilibria in soil profiles from the southeastern Australian highlands

Abstract

The sustainability of soil resources is determined by the balance between the rates of production and removal of soils. Samples from four weathering profiles at Frogs Hollow in the upper catchment area of the Murrumbidgee River (southeastern Australia) were analyzed for their uranium-series (U-series) isotopic composition to estimate soil production rates. Sequential leaching was conducted on sample aliquots to assess how U-series nuclides are distributed between primary and secondary minerals. Soil is increasingly weathered from bottom to top which is evident from the decrease in ($^{234}\text{U}/^{238}\text{U}$) ratios and increase in relative quartz content with decreasing soil depth. One soil profile shows little variation in mineralogy and U-series geochemistry with depth, explained by the occurrence of already extensively weathered saprolite, so that further weathering has minimal effect on mineralogy and geochemistry. Al_2O_3 is mobilized from these soils, and hence a silicon-based weathering index treating Al_2O_3 as mobile is introduced, which increases with decreasing soil depth, in all profiles. Leached and unleached aliquots show similar mineralogy with slight variation in relative concentrations, whereas the elemental and isotopic composition of uranium and thorium show notable differences between leached and unleached samples. Unleached samples show systematic variations in uranium-series isotopic compositions with depth compared to leached samples. This is most likely explained by the mobilization of U and Th from the samples during leaching. Soil residence times are calculated by modeling U-series activity ratios for each profile separately. Inferred timescales vary up to 30 kyr for unleached aliquots from profile F1 to up to 12 kyr for both leached and unleached aliquots from profile F2. Muscovite content shows a linear relationship with U-series derived soil residence times. This relationship provides an alternative method to estimate residence timescales for profiles with significant U-series data scatter. Using this alternative approach, inferred soil residence times up to 33 kyr for leached samples of profile F1 and up to 34 kyr for leached samples of profile F3 were determined. A linear relationship between soil residence times and WIS (Si-based Weathering Index) exists and is used to estimate soil residence times for profile F3 (up to 28 kyr) and F4 (up to 37 kyr). The linear relationship between soil depth and calculated residence time allows determination of soil production rates, which range from 10 to 24 mm/kyr and are comparable to the rates determined previously using cosmogenic isotopes at the same site (Heimsath et al., 2001b). This implies that at this site, on the highland plateau of southeastern Australia, soil thickness has reached steady-state, possibly as a result of stable tectonic conditions but despite variable climatic conditions over the timescale of soil development. Soil-mantled landscapes are the geomorphic expression of this balance between soil production and denudation, and our results show that in tectonically quiescent regions, this landscape can be achieved in less than 30 kyr.

Keywords

series, isotope, disequilibria, profiles, southeastern, uranium, australian, soil, highlands, determined, rates, formation

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

---

Publication Details

Suresh, P. O., Dosseto, A., Hesse, P. P. & Handley, H. K. (2013). Soil formation rates determined from Uranium-series isotope disequilibria in soil profiles from the southeastern Australian highlands. *Earth and Planetary Science Letters*, 379 26-37.

1   **Soil Formation Rates Determined from Uranium-Series Isotope Disequilibria in**
2   **Soil Profiles from the South-eastern Australian Highlands**

6   **P. O. Suresh^{1*}, A. Dosseto², P. P. Hesse¹, H. K. Handley³**

8   ¹Department of Environment and Geography, Macquarie University, Sydney, Australia

9   ²GeoQuEST Research Centre, School of Earth and Environmental Science, University of Wollongong,
10   Australia

11   ³GEMOC, Department of Earth and Planetary Sciences, Macquarie University, Sydney, Australia

13   * Corresponding author: suresh.puthiyaveetil-othayoth@mq.edu.au

14   Phone: +61-2-9850-8396

15   Fax: +61-2-9850-8420

Abstract

The sustainability of soil resources is determined by the balance between the rates of production and removal of soils. Samples from four weathering profiles at Frogs Hollow in the upper catchment area of the Murrumbidgee River (southeastern Australia) were analyzed for their uranium-series (U-series) isotopic composition to estimate soil production rates. Sequential leaching was conducted on sample aliquots to assess how U-series nuclides are distributed between primary and secondary minerals. Soil is increasingly weathered from bottom to top which is evident from the decrease in ($^{234}\text{U}/^{238}\text{U}$) ratios and increase in relative quartz content with decreasing soil depth. One soil profile shows little variation in mineralogy and U-series geochemistry with depth, explained by the occurrence of already extensively weathered saprolite, so that further weathering has minimal effect on mineralogy and geochemistry. Al_2O_3 is mobilized from these soils, and hence a silicon-based weathering index treating Al_2O_3 as mobile is introduced, which increases with decreasing soil depth, in all profiles. Leached and unleached aliquots show similar mineralogy with slight variation in relative concentrations, whereas the elemental and isotopic composition of uranium and thorium show notable differences between leached and unleached samples. Unleached samples show systematic variations in uranium-series isotopic compositions with depth compared to leached samples. This is most likely explained by the mobilization of U and Th from the samples during leaching. Soil residence times are calculated by modeling U-series activity ratios for each profile separately. Inferred timescales vary up to 30 kyr for unleached aliquots from profile F1 to up to 12 kyr for both leached and unleached aliquots from profile F2. Muscovite content shows a linear relationship with U-series derived soil residence times. This relationship provides an alternative method to estimate residence timescales for profiles with significant U-series data scatter. Using this alternative approach, inferred soil residence times up to 33 kyr for leached samples of profile F1 and up to 34 kyr for leached samples of profile F3 were determined. A linear relationship between soil residence times and WIS (Si-based Weathering Index) exists and is used to estimate soil residence times for profile F3 (up to 28 kyr) and F4 (up to 37 kyr). The linear relationship between soil depth and calculated residence time allows determination of soil production rates, which range from 10 to 24 mm/kyr and are comparable to the rates determined previously using cosmogenic isotopes at the same site (Heimsath et al., 2001). This implies that at this site, on the highland plateau

of southeastern Australia, soil thickness has reached steady-state, possibly as a result of stable tectonic conditions but despite variable climatic conditions over the timescale of soil development. Soil-mantled landscapes are the geomorphic expression of this balance between soil production and denudation, and our results show that in tectonically quiescent regions, this landscape can be achieved in less than 30 kyr.

Keywords

Soil production, uranium-series isotopes, climate variables, landscape evolution

1. Introduction

The availability of soil resources depends on the balance between soil production via weathering and loss by erosion. If the soil production rate is greater than or equal to the erosion rate, the soil resource is sustainable. In a compilation and review of soil production and erosion rates estimated for various climatic and geological settings, Montgomery (2007) reports an imbalance between agricultural soil loss and replenishment of soil resulting in a net soil loss; raising a concern for the availability of sustainable soil resources. To estimate soil production rates and therefore assess soil sustainability it is necessary to quantify the soil residence time, i.e. the time elapsed since conversion of saprolite or bedrock into soil.

Until recently, soil production rates were difficult to quantify, inferred from weathering rates by methods using stream water and sediment chemistry (Owens and Watson, 1979a, 1979b; Pavich, 1989; Wakatsuki and Rasyidin, 1992; Treoh, 2004). These studies relied on assumptions such as homogeneous bedrock composition or unvarying stream water composition representative of solute abundance over the timescale of soil development (Alexander, 1998; Owens and Watson, 1979a, 1979b). Over the past few years, two new techniques have emerged that have significantly improved our ability to quantify rates of soil production. Firstly, the measurement of cosmogenic nuclides in the material underlying the soil (saprolite or bedrock) can be used to determine soil denudation rates. Assuming a constant soil thickness over time, soil production rates can be determined as they are equal to denudation rates

(Heimsath et al., 2001, 2000). However, this technique cannot be used to ascertain imbalances between soil production and loss since both processes are assumed to operate in equilibrium. Secondly, uranium-series (U-series) isotopic compositions of soil/saprolite material in a depth profile can be modeled to quantify the residence time of weathered material within the profile (*soil or saprolite residence time*). This method is based on the principle that the U-series isotopes fractionate during chemical weathering and their abundance is time-sensitive due to their radioactive nature (e.g. Chabaux et al., 2003, 2013; Ma et al., 2010, 2013; Dosseto et al., 2008a, b, 2012; Dequincey et al., 2002). For a system that has remained closed for more than 1 Myr, all daughter-parent activity ratios of the uranium decay chains (e.g. $(^{234}\text{U}/^{238}\text{U})$ or $(^{230}\text{Th}/^{234}\text{U})$; parentheses denote activity ratios throughout this article) will be equal to 1. This is termed *secular equilibrium*. The implication is that for a parent rock older than 1 Myr, its U-series isotopic composition is known; it will be in secular equilibrium irrespective of the lithology. During soil formation, U-series isotopes fractionate, creating *radioactive disequilibrium* between parent-daughter nuclide pairs. ^{234}U is preferentially mobilized compared to ^{238}U as a result of two processes: (i) the recoil loss of ^{234}Th from mineral grains due to the decay of ^{238}U within a few 10's of nm of the grain surface, and subsequent decay of ^{234}Th into ^{234}U in the surrounding medium (Kigoshi, 1971); (ii) preferential leaching of ^{234}U located in radiation-damaged crystal sites from which it can be easily mobilized. Thus, $(^{234}\text{U}/^{238}\text{U})$ activity ratios < 1 should be observed in soils. Fractionation between U (^{234}U , ^{238}U) and ^{230}Th occurs as a result of the difference in their solubility. Oxidizing conditions prevail in most soils and so U will be present as U^{6+} , which is soluble in waters as the uranyl ion, $\text{U}_{\text{VI}}\text{O}_2^{2+}$, is stabilized by highly soluble and non-reactive carbonate complexes (Langmuir, 1978). Th will be present as Th^{4+} , which is insoluble. As a result, we expect $(^{230}\text{Th}/^{234}\text{U})$ ratios > 1 in weathering profiles. Once radioactive disequilibrium is produced, a given parent-daughter system will return to secular equilibrium governed by natural radioactive decay over a timescale equivalent to approximately 5 half-lives of the daughter isotope. Thus, the $(^{230}\text{Th}/^{234}\text{U})$ activity ratio will attain secular equilibrium in ~ 400 kyr, whereas it will take a million years for $(^{234}\text{U}/^{238}\text{U})$. Addition of isotopes of U or Th due to processes such as illuviation, dust deposition, lateral transport or bioturbation will also contribute to the U-series isotope composition of soils and this needs to be taken into account when modeling

U-series isotopic composition of weathering profiles (Chabaux et al. 2008; Dequincey et al. 2002).

The U-series approach has been used by Dosseto et al. (2008a) to study soil production rates on the escarpment of the eastern side of the Great Dividing Range in southeastern Australia. The reported soil production rates ranging from 12 to 77 mm/kyr are comparable to the range of denudation rates given by Heimsath et al. (2000) (10 to 50 mm/kyr). In this study, we apply the U-series approach to soil profiles at Frogs Hollow in the highlands (Fig. 1a), west of the escarpment site studied by Dosseto et al. (2008a). Compared to the escarpment area, the highland region is characterized by lower relief, erosion rates, mean annual temperature and rainfall. Pleistocene periglacial effects may also have been more important in the highlands, compared to the escarpment (Galloway, 1965; Barrows et al. 2002). At the Frogs Hollow study site, Heimsath et al. (2001) determined soil production rates using cosmogenic nuclides ^{26}Al and ^{10}Be . With an assumption of constant soil thickness over time, the determined soil production rates vary from 10 mm/kyr for 70 cm-thick soil profiles to 50 mm/kyr for 20 cm-thick profiles, with soil production rate inversely related to soil thickness and slope curvature. Heimsath et al. (2001) tested the steady-state soil thickness assumption by measuring a cosmogenic nuclide profile in a protruding tor. However, although this experiment constrains how soil is being denuded (and Heimsath et al. (2001) show that at this site, soil was stripped during a rapid event more than 150 kyr ago), it does not allow determination of how soil thickness has evolved through time. Here, we use U-series isotopes measured in soil and saprolite material as an alternative approach to infer soil production rates, and compare the results to those of Heimsath et al. (2001). The advantage of the U-series isotope technique is that steady-state soil thickness is not a required assumption, although other assumptions are needed and these are presented below. Comparing the soil production rates estimated from soil residence times determined using U – series activity ratios of soil profiles from Frogs Hollow with those determined using cosmogenic radionuclides (Heimsath et al., 2001) is expected to put insight into the sustainability of soil mantled landscape at the studied site.

Yoo et al. (2007) developed a model to study timescales of soil transport on hill slopes, combining chemical weathering and physical erosion. One of the

important requirements for the model is the determination of soil residence time due to soil production from bedrock. To apply their model to estimate hill slope soil transport time at Frogs Hollow, Yoo et al. (2007) used the soil production rates determined by Heimsath et al. (2001), which are inferred from soil denudation rate. The U-series isotope method discussed here gives a more direct method for determining soil residence time.

2. Field description

Frogs Hollow is a small area (0.04 km²) in the upper catchment of the Murrumbidgee River (Fig. 1). The river flows from the Great Dividing Range of south-eastern Australia towards the west, where it joins the Murray River and flows into the Southern Ocean. The study locality at Frogs Hollow is at an elevation of 930 m, 80 km south–southeast of Canberra, 75 km from the coast, and ~ 12 km west of the eastern escarpment (Fig. 1a). A detailed site description is given by Heimsath et al. (2001). The underlying bedrock at this site is Devonian granite (Richardson, 1976). The average summer temperature is 19°C and the average winter temperature is 5°C. Annual average rainfall is 500 mm (Bureau of Meteorology, NSW, 2010). Patches of dry sclerophyll woodland are present above a grass understory. Samples were collected from four pits (F1-F4) dug at the most convex points on ridge tops, and were taken from both sides of a colluvial hollow to avoid any contribution from laterally transported soil (Fig. 1b). Profiles F1 and F2 are on the western ridge, where F2 is located 80 m south of F1 and 6 m lower in elevation. Profiles F3 and F4, on the eastern ridge of the hollow, are 100 m apart and F4 is at an elevation 3 m lower than that of F3. The two ridges are ~75 m apart.

Samples were collected at 8 cm intervals by inserting a cylindrical steel pipe horizontally into the pit wall. The four soil profiles were chosen on the basis that they replicate the same geomorphic and pedological conditions: high convexity on top of the ridges (Figure 1). The expectation was that they would replicate profile properties and residence times. However, several differences in profile thickness, horizon properties and mineralogy were observed during sample collection (Figures 1, 2 and 3). These differences could represent small variations in slope curvature (see Heimsath et al., 2001) or substrate composition. Soil depths vary from 30 to 48 cm

above the saprolite. Three of the pits (F2, F3 and F4) have similar overall thickness, while profile F1 is significantly thicker. Nevertheless, all four profiles show variable individual horizon thicknesses and textures. All the soils are acidic, with pH varying from 5 to 6.5.

3. Analytical techniques

U-series isotopes of aliquots of the $< 53 \mu\text{m}$ size fraction of the soil samples were analyzed following the procedure described in Sims et al. (2008) and Turner et al. (2011). In order to assess the effect of organic matter and secondary phases on U-series isotopes of soils, another set of sample aliquots ($< 53 \mu\text{m}$) were subjected to a sequential extraction and clay separation procedure described by Suresh et al. (under revision) for U-series analysis (Table A.1, Supplementary Materials) (The latter set of aliquots containing only primary mineral fractions are referred to as “leached” samples hereafter). Accuracy was determined by analyzing the TML-3 rock standard and measured values are within published values by 1.1% for Th concentration, 0.06% for U concentration, and 0.6% for ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) ratios (Table 1). Total procedural blanks were typically 70 pg for Th and 20 pg for U. Sample mineralogy was determined using XRD technique. Major elements concentrations were determined using XRF method. A detailed description of analytical methods used is given in the supplementary materials.

4. Model of U-series isotope evolution in weathering profiles

The magnitude of the radioactive disequilibrium created during chemical weathering is a function of the extent of chemical weathering and time. Therefore, the measurement of disequilibrium in weathering products can be used to constrain the timescales of chemical weathering. Vigier et al. (2001) and Dosseto et al. (2006) modeled the time variation of any given nuclide as a function of its production by decay of the parent (if present) and its loss through subsequent decay and weathering. This model was further modified to incorporate possible additions of nuclides, for instance due to illuviation, the precipitation of secondary phases, or dust deposition (Dosseto et al., 2008a, b; Dequincey et al., 2002). This model considers that the U-series disequilibrium present in the soil is due to chemical weathering only.

According to this model, the abundance of a daughter nuclide in the weathering profile varies with time as follows:

$$dN_j/dt = \lambda_i N_i - \lambda_j N_j - k_j N_j + f_j N_{j,0} \quad (1)$$

where subscripts i and j refer to the parent and daughter nuclides, respectively, λ is the decay constant (yr^{-1}), $N_{j,0}$ is the initial nuclide abundance, f and k are input and dissolution coefficients, respectively (in yr^{-1}). The gain coefficient, f , is a time constant at which the input of a radionuclide occurs via dust deposition and/or chemical illuviation, and the dissolution coefficient k , at which removal of the radionuclide occurs due to chemical weathering. In the case of soil production from saprolite, the time required for the U-series isotopic composition of the saprolite to evolve to that of a given soil sample is calculated. In other words, this term represents the soil residence time. For ^{238}U , equation (1) can be written as

$$d^{238}\text{U}/dt = -\lambda_{238} \times ^{238}\text{U} - k_{238} \times ^{238}\text{U} + f_{238} \times ^{238}\text{U}_0 \quad (2)$$

Similarly, for ^{234}U

$$d^{234}\text{U}/dt = \lambda_{238} \times ^{238}\text{U} - \lambda_{234} \times ^{234}\text{U} - k_{234} \times ^{234}\text{U} + f_{234} \times ^{234}\text{U}_0 \quad (3)$$

and for ^{230}Th ,

$$d^{230}\text{Th}/dt = \lambda_{234} \times ^{234}\text{U} - \lambda_{230} \times ^{230}\text{Th} - k_{230} \times ^{230}\text{Th} + f_{230} \times ^{230}\text{Th}_0 \quad (4)$$

The model can be solved for a given profile to determine the set of k and f values for each nuclide and the residence time (T_{res}) of each sample by reproducing observed ($^{230}\text{Th}/^{234}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$) activity ratios. The gain (f) and dissolution (k) coefficients can take different values for each nuclide, and are considered to be constant for a given soil profile and over time. T_{res} is expected to increase with decreasing soil depth. The model constrains k and f values for each profile and T_{res} values for each sample that reproduce the measured isotopic compositions. A detailed description of the model is given in Dosseto et al. (2008a), Dosseto et al. (2012) and Chabaux et al. (2013).

5. Results

5.1. Mineralogy

The four profiles (F1-F4) are dominated by primary minerals (quartz, microcline, albite and muscovite), reflecting the mineralogical composition of the underlying granitic bedrock (Supplementary Materials - Table A.2). In profiles F1, F2 and F3 both the leached and unleached samples show an increase in quartz content and a decrease in muscovite content with decreasing depth (Fig. 2)(Supplementary Materials, Fig. A.1, Table A.2). In profile F4, leached samples show high quartz contents and low albite and microcline contents compared to the other profiles (Supplementary Materials, Fig. A.1). Muscovite is detected in the saprolite only (< 2% by mass). No significant variation was observed in the mineralogy throughout the profile.

5.2. Major elements

For profile F1, F3 and F4 SiO_2 content increases from the saprolite the top soil, while Al_2O_3 content decreases with decreasing depth, reflecting the changes in mineralogy (Supplementary Materials, Table A.3). Fe_2O_3 decreases from the saprolite to the top soil. K_2O does not show significant variation with depth. CaO and Na_2O increase with decreasing depth. Other major elements are present in less than 1 wt %. For profile F2, only one soil sample (F2c) and the saprolite sample were analyzed for major elements. For profile F4, all the samples show high SiO_2 concentrations, reflective of its quartz-rich mineralogy.

5.3. Uranium-series isotopes

In profile F1, unleached and leached samples show similar ranges of U concentration, whereas Th concentrations are higher in the unleached than those of the leached samples (Table 1). In profile F2, unleached samples show higher U and Th concentrations compared to leached samples (Table 1). This suggests a loss during leaching of 9 to 37% for U and 20 to 60% for Th in profile F1, and 36 to 44% for U

and around 36% for Th in profile F2. These values are attributed to the removal during leaching of U- and Th-bearing primary minerals in the < 2 μm size fraction and/or secondary minerals present in levels undetectable by XRD.

The leached and unleached samples of profiles F1, F2 and F3 show a general decrease in U and Th concentration with decreasing depth (Fig. 3a & b). Similar to the mineralogical data, U and Th concentrations show less variation in profile F4. These variations suggest a loss of U and, to a lesser extent, of Th during soil development. Although this is expected for U, it is surprising for Th and could be the result of its mobilization by organic acids in the soil (Chabaux et al., 2003). As depth decreases, all profiles show an inflection to higher Th concentration at 12cm depth (except for F1 unleached samples) followed by a decrease into the topsoil. In profiles F2, F3 and F4, soils are characterized by similar U/Th ratios, with values lower or similar to that in the saprolite (Supplementary Materials, Fig. A.2), suggesting that U is more readily mobilized than Th. In profile F1, soil U/Th ratios are higher than that of the saprolite. This is mostly accounted for by higher Th concentrations in the saprolite compared to that in the soil (Fig. 3b). In all profiles, the soil samples show an overall decrease in ($^{234}\text{U}/^{238}\text{U}$) and increase in ($^{230}\text{Th}/^{234}\text{U}$) with decreasing depth (Figs. 3c & d). This indicates an increasing depletion of ^{234}U over ^{238}U and ^{230}Th during soil development. Moreover, in profiles F1, F2 and F3, ($^{234}\text{U}/^{238}\text{U}$) ratios are negatively correlated with quartz content (not shown). This illustrates the increasing depletion of ^{234}U with the increasing extent of chemical weathering (increasing quartz content). These patterns are consistent for both leached and unleached samples in profiles F1 and F2.

6. Discussion

6.1. Mineralogical, geochemical and isotopic variations in the weathering profiles

In an undisturbed soil profile, the residence time of soil and the extent of weathering are expected to increase with decreasing depth. White et al. (1996) reported an increase in soil median grain size with increasing soil age, suggesting the dependence of soil grain size distribution on size reduction and complete dissolution of smaller grains due to chemical weathering. The observed increase in median grain

size with decreasing soil depth at Frogs Hollow signifies the increase of soil residence time and extent of weathering with decreasing depth. Illuviation of finer particles from topsoil to bottom may also produce this trend. However, illuviation should also influence the weathering index of the soil. The linear increase of the Si-based Weathering Index (WIS, discussed later in this section) rules out the possibility of illuviation. The possibility of sorting of minerals by bioturbation also can be ruled out at this location, based on the observation of well-defined horizon boundaries and negligible bioturbation rates (discussed later in this section).

The leached and unleached samples of a given profile show similar mineralogical trends for quartz, albite, muscovite and microcline. Secondary minerals were not detected by XRD. Moreover, the leaching procedure does not seem to significantly affect the distribution of primary minerals. All profiles (except F4) show an increase in quartz content and decrease in muscovite content with decreasing depth consistent with increased chemical weathering from the bottom to the top of the profiles. The decrease in muscovite content from the saprolite to the topsoil in leached and unleached samples of profiles F1, F2 and leached samples of F3 suggests that (i) this mineral survives saprolite formation, and (ii) it is steadily dissolved during saprolite breakdown into soil. This is also observed in profile F4, where muscovite is present in the saprolite but not the soil. Dissolution of muscovite is enhanced if mildly acidic organic acid is present in the soil (Oelkers et al., 2008). The fact that secondary precipitates of dissolved muscovite were not detected by XRD in any of the samples suggests that precipitation of detectable levels of secondary minerals from dissolved muscovite are unlikely, as observed by Rosenberg and Kittrick (1990), at temperature and pressure conditions akin to Frogs Hollow. The weathering rates of feldspar minerals strongly depend on their specific surface area (Stillings et al., 1996). Muscovite has a higher surface to volume ratio than albite and microcline and will therefore be less resistant to weathering, and may explain the observed decrease of muscovite content and invariance of albite and microcline content with decreasing soil depth at Frogs Hollow.

The lack of significant mineralogical variation in profile F4, compared to other profiles, could be due to evolution of the soil from a highly weathered saprolite, from which most of the weatherable materials had already been removed. This is supported

by the high quartz content and low muscovite content in the F4 saprolite. The subsequent weathering processes in the soil may have only a minimal amount of weatherable material available to dissolve, which in turn gives rise to minimal variations in U-series elemental and isotopic composition as well as in mineralogy throughout the profile. On the contrary, the saprolite from profile F1 contains the least amount of quartz, suggesting a lower extent of weathering of the saprolite in that profile. Quartz content sharply increases during the conversion of saprolite into soil in profile F1 compared to all other profiles, indicating heterogeneity in soil and saprolite weathering at a very local scale. This heterogeneity may be related to preferential weathering at bedrock joints, which led to the formation of the existing tors at Frogs Hollow.

The decrease of muscovite and Al_2O_3 concentrations with depth and the absence of secondary Al-bearing minerals suggest mobilization of Al in these soils. When mildly acidic conditions prevail in soil, such as observed in Frogs Hollow (pH between 4 and 6), mobilization of Al_2O_3 occurs (Driscoll et al., 1985; White, 2008). Commonly used weathering indices (CIA or CIW) consider Al as an immobile phase, and these indices were found not to be applied to the soil samples at Frogs Hollow. By contrast, SiO_2 in Frogs Hollow soil is comparatively immobile, which is evident from its increasing concentration with decreasing depth and the parallel increase of quartz content with decreasing depth. We use a Si-based Weathering Index (WIS) which considers SiO_2 as the immobile phase instead. It is written as

$$\text{WIS} = \text{SiO}_2 / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O}) \quad (5)$$

Index values increase with increased weathering intensity. Calculated WIS values are shown in Table 1. For all the profiles, WIS increases with decreasing depth, again indicating that chemical weathering intensity increases with decreasing soil depth (Fig. 4). For profiles F1, F2 and F3, WIS values vary between 61 to 77 % with depth, and for profile F4 values are significantly higher, increasing from 78 % to 84 %, indicating that the soil in this profile has undergone more weathering than other profiles.

Uranium is mobile in soil during weathering under oxidizing conditions due to the high solubility of U^{6+} ions. Organic acids in the soil will also enhance the solubility of U (Chabaux et al., 2003). The relatively acidic soil pH (5 to 6) at Frogs Hollow suggests that organic acids in the soil may account for the decrease in U concentration with decreasing soil depth. Thorium is relatively less mobile than U in soils. However, organic acids within soils can also increase its mobility (Hansen and Huntington, 1969; Langmuir and Herman, 1980; Tylor and Olsson, 2001; Chabaux et al., 2003). At pH 5 to 6, the solubility of thorium is a few orders of magnitude higher than that at pH 7 and above (Langmuir and Herman, 1980). Therefore, the observed decrease in Th concentration with decreasing soil depth at Frogs Hollow could also be attributed to soil acidity. The inflection in Th concentration at 12 cm depth in all soil profiles may be related to the higher clay to silt ratio at the same depth (Supplementary Materials, Table A.4). When normalized to the values of corresponding saprolites, Th concentrations and clay to silt ratios are positively correlated ($R^2 > 0.9$) for profiles F2, F3 and F4 and for samples below 16 cm depth from profile F1. Similarly, U concentrations are also positively correlated ($R^2 > 0.88$) with clay to silt ratio. This is consistent with the observation that the concentration of radioactive elements increases with decreasing soil grain size (Baeza et al. 1995). The lowest clay to silt ratio value observed for the top soil in profile F1 (0.022) may be an indication of extensive removal of clay-sized particles from the top soil by chemical dissolution.

The mobility of U-series isotopes is expected to be as follows: $^{234}U > ^{238}U \gg ^{230}Th$. As the extent of weathering increases, ^{234}U will be removed from the soil more easily than ^{238}U and ^{230}Th . Hence $(^{234}U/^{238}U)$ ratios are expected to decrease and $(^{230}Th/^{234}U)$ ratios to increase in weathering profiles with decreasing soil depth (Dequincey et al., 2002; Dosseto et al., 2008a; Dosseto et al., 2012), which is observed here (Figs. 3c & d). The anomalously low $(^{234}U/^{238}U)$ and high $(^{230}Th/^{234}U)$ activity ratios in the saprolite sample of profile F1 (compared to the trends of the other profiles), may be due to a lesser degree of weathering in that saprolite, hence recording activity ratios of early stages of evolution of U-series isotopes during weathering.

6.2 Soil Residence Time

6.2.1 U-Series Model

As explained above, it is possible to use measured activity ratios of U-series isotopes in soils to place constraints on the mobility of radionuclides during soil formation and to determine the time elapsed since production from the saprolite, i.e. the soil residence time. Equation (1) is solved for ^{238}U , ^{234}U and ^{230}Th using Matlab to reproduce the observed ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) activity ratios in the soil samples. The activity ratios and elemental concentrations in the saprolite are taken to represent the initial conditions. The leaching and input coefficients are assumed to be constant for each radionuclide in a given profile. A second assumption is that the timescale over which the gain of nuclide via illuviation and/or dust input occurs over a similar timescale to nuclide loss. The current model does not have enough constraints to tackle the possibilities of these processes occurring over different timescales.

The model generates activity ratios for a given sample, evolved from the given initial conditions of the saprolite. These ratios are then compared with the measured activity ratios from the sample, and the activity ratio generated is iterated to seek the set of parameters t , k_{230} , k_{234} , k_{238} , f_{230} , f_{234} and f_{238} that best reproduce the observed activity ratios. Since the system of equations to be solved is strongly non-linear, a large number of solutions sets are generated from which the median is retained as the best set of parameters. The error on each parameter is determined by calculating the standard error on the population of solutions generated.

The model was solved for unleached samples of profiles F1 and F2, and for leached samples of profile F2. Leached samples of profiles F1, F3 and F4 gave t values of over a million years, which lead to unrealistically slow soil production rates, and so those results were discarded. Leaching of the samples may have affected the U-series isotope composition introducing scatter in the activity ratio data, which could account for the unrealistic modeling results. Soil being a complex mixture of different phases, redistribution of U-series isotopes to different phases during sequential extraction is possible, which then could lead to data scatter. U and Th are removed from the samples of both F1 and F2 during leaching, but the amount of Th removed from profile F1 is not as consistent as that removed from profile F2, and U removed

from both the profiles (Supplementary Materials, Fig. A.3a). Readsorption of Th during leaching could have occurred during leaching. The ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) activity ratios are also scattered unevenly during leaching (Supplementary Materials, Fig. A.3b). Readsorption of trace elements during sequential extraction of phases from soil has been reported by Gleyzes et al. (2002) also. It is worth pointing out that the residence times determined for leached and unleached fractions of soil from profile F2 yield similar values. Although the variation of activity ratios of U-series isotopes with depth for the leached and unleached aliquots of other profiles does not follow the same trends, their relative mineral concentrations are similar. This interrelation is discussed further in subsequent sections.

Calculated k and f values for each nuclide are shown in Table A.5 (Supplementary Materials). Their ranges are similar to previously published values for soils and river sediments (Vigier et al., 2001; Dequincey et al., 2002; Dosseto et al., 2008a). The k values for ^{238}U and ^{234}U for unleached samples in profiles F1 and F2 are greater than those inferred for leached samples of profile F2, suggesting that the presence of a clay-sized primary mineral fraction ($< 2 \mu\text{m}$) or secondary minerals, even if at an undetectable level, could significantly influence the estimation of U isotope dissolution rates. Unleached samples yield k values for ^{230}Th isotope that are comparable to or greater than those of ^{238}U . However, modeling of the leached samples indicates negligible loss of ^{230}Th . The results also suggest that the rates of addition and removal of ^{238}U are similar. For profile F2, the calculated f value for ^{234}U in unleached samples is greater than that calculated for leached samples.

Leaching coefficients of U and Th isotopes in the unleached samples are an order of magnitude lower than those reported by Dosseto et al. (2008a) ($\sim 1.5 \times 10^{-4}$) for soils developed over similar bedrock lithology but located at the retreating escarpment, east of the study site. This could be explained by higher rates of chemical weathering -promoted by faster erosion rates at the escarpment compared to that at the highland plateau (Heimsath et al., 2010). In contrast, gain coefficients are similar for both sites. Dequincey et al. (2002) reported similar dissolution and gain rates of U-series isotopes from soils formed over similar bedrock lithology in a tropical climate ($\sim 10^{-5}$). Also, soil developed over shale bedrock, but under similar climate conditions

to Frogs Hollow showed U-series leaching coefficients similar to those reported here (Ma et al., 2010).

Calculated soil residence times are shown in Table 2. In profile F1, residence time varies from 15.9 ± 1.9 to 30.3 ± 3.6 kyr with decreasing soil depth. In profile F2, both the leached and unleached fractions give similar residence times, varying between 2.2 ± 1.7 and 13.6 ± 4.8 kyr for the unleached fraction and 3.2 ± 1.8 to 11.8 ± 5.9 kyr for the leached fraction, with decreasing depth. Extrapolating the data to the soil-saprolite boundary gives ages of 3.9 ± 3.4 kyr (F1 unleached) and 1.5 ± 1.4 kyr (F2) for the base of the soil profile. Thus, although the sample leaching seems to significantly affect the estimation of dissolution and input rates for the different nuclides considered, they do not seem to affect calculated soil residence timescales. Using the negative relationship between soil depth and residence time, it is possible to calculate an average soil production rate using a simple linear regression (Fig. 5). Profile F1 unleached samples yield an average soil production rate of 15 ± 5 mm/kyr (Fig. 5a). For profile F2, leached and unleached fractions yield average soil production rates of 24 ± 5 and 18 ± 8 mm/kyr, respectively (Fig. 5b). Note that the measured U-series isotope compositions from only 3 out of 6 soil profiles could be used to infer soil residence times and production rates, illustrating the complex processes involved during soil formation. Nevertheless, the presence of clay-sized ($< 2 \mu\text{m}$) primary minerals or secondary phases do not appear to significantly affect the soil production rates estimated, since calculation using unleached or leached samples from profile F2 yield similar values. The calculated soil production rates are similar to those reported by Heimsath et al. (2001) calculated using cosmogenic isotopes for the same site, which validates the assumption of a steady-state soil thickness that is used in the cosmogenic isotope method.

6.2.2. Muscovite Content and Soil Residence Time

In the model developed to estimate chemical weathering and transport of soil in hillslopes, Yoo et al. (2007) propose the inter-dependence of soil weathering and soil residence time. Muscovite contents in unleached samples from profiles F1 and F2 and leached samples from profile F2 show a linear relationship with the calculated soil residence time (Fig. 6a). Interestingly, the slope for the three data series is similar,

with values between -0.71 and -0.94. Thus, the mean slope of the three linear regression lines (-0.84; Fig. 6a) is used to estimate the soil residence times for profiles F1 and F3, using the muscovite content of their leached samples in the following equation:

$$T_{\text{res}} = (\text{Mu}_{\text{sap}} - \text{Mu}_{\text{soil}})/0.84 \quad (6)$$

where Mu_{soil} is the mass percentage of muscovite in the soil and Mu_{sap} is that in the underlying saprolite. T_{res} is the residence time in kyr. The calculated residence times vary from 2.9 ± 1.4 to 32.8 ± 16.4 kyr for profile F1 and 15.1 ± 7 to 33.6 ± 16.8 kyr for profile F3 (Table 2). Extrapolating the data to the soil-saprolite boundary gives residence times of 0 kyr (F1 leached) and 8.3 ± 3 kyr (F3 leached) for the base of the soil profile. These residence time values are comparable to those of the other profiles directly inferred from the modeling of U-series isotope compositions. Here too a linear relationship is observed between soil residence time and depth, which can be used to calculate average soil production rates. It yields 13 ± 2 mm/kyr for leached samples of profile F1 and 10 ± 1 mm/kyr for leached samples of profile F3 (Fig. 6b). These production rates are comparable to those determined from modeling U-series isotope composition (Fig. 5). Equation (8) could not be applied to profile F4 as muscovite was not detected in the soil.

6.2.3. WIS and Soil Residence Times

The Si-based Index of Weathering (WIS) and the soil residence time determined using U-series isotopes for profile F1 shows a linear relationship (Fig. 7a). Similarly to equation (6), an equation for T_{res} can be deduced:

$$T_{\text{res}} = 1.3 \times \text{WIS} \quad (7)$$

This equation is used to estimate residence times of soils in profiles F3 and F4. The soil residence times vary from 20.3 ± 13.9 to 28.5 ± 14.5 kyr for profile F3 and from 33.0 ± 14.9 to 37.2 ± 15.2 kyr (Table 2). The linear relationship between soil depth

and residence time is used to estimate soil production rates of 29 ± 3 and 52 ± 18 mm/kyr for profile F3 and F4 respectively (Fig. 7b).

Mass loss due to chemical weathering during soil transport down the hill slope was modeled by Yoo et al. (2007), combining soil residence time due to soil production from bedrock and soil residence time driven by lateral mass transport. Soil residence time on the ridge tops at Frogs Hollow reported in this work is consistent with that determined by Yoo et al. (2007) (21 kyr), which assumed soil depth-production rate values determined by Heimsath et al. (2001). Yoo et al.'s model suggested that in addition, it takes ~60 kyr for soil to be transported ~50 m down slope to the hollow, indicating a longer residence time of soil in this small catchment. The soil residence times determined here, using U-series isotopes which are independent of the assumption of steady state soil depth or soil depth- production rate relationship, give an independent estimate of timescales of soil transport through hill slopes, even in areas where soil thickness is not in steady state.

The discovery of consistent chemical weathering profiles within the topsoil profiles implies that chemical weathering-driven soil production is occurring at faster rates than biological turnover, which would otherwise homogenize the soil and destroy the geochemical trends. Multiplying the soil production rate with the bulk density of soil (assumed to be 1.1 g/cm^3) yields an upper limit for the rate of biological soil mixing at this location (Supplementary Materials, Table. A.6). The highest value calculated for Frogs Hollow ($26.4 \pm 5.5 \text{ g/m}^2/\text{year}$) is less than one third of the lowest rate ($94 \text{ g/m}^2/\text{year}$) determined for Nattai National Park footslopes, in a lower elevation and higher rainfall environment near Sydney, using optical luminescence dating of soil (Richards, 2009).

6.3. Implications

Bedrock lithology may have a major role in soil production processes (Table 3). Ma et al. (2010, 2013) reported soil production rate ~45 mm/ kyr over shale lithology at Sasquehanna Shale Hills Critical Zone Observatory. In the tropical settings of Puerto Rico, at the Bisley 1 research catchment in the Liquillo Mountains with andesitic volcanoclastic bedrock, a soil production rate of ~400 mm/kyr is

reported by Dosseto et al. (2012). For an adjacent catchment (Rio Icacos) where the bedrock lithology is quartz diorite, Chabaux et al. (2013) reported a soil production rate of 45 mm/kyr. A compilation of soil production rates determined using U – series isotopes also showed that soil production rate over granitic lithology are in the same range (Dosseto et al., 2012).

Temperature, elevation, slope and seismicity appear to have minimum influence on soil production rates (Table 3). No reliable correlation has been observed between these parameters and soil production rates. Portenga and Bierman (2011) reported strong positive correlation between basin slope and erosion rates, at the global scale. The authors also report that mean elevation, relief and seismicity are also significantly correlated with erosion rates. The data compiled in Table 3 shows that rainfall and relief are strongly correlated with soil production rates ($R = 0.86$ and 0.95 respectively) (Supplementary Materials, Fig. A.4). Despite the limited data available to make global comparisons of soil production rates, it can be inferred that rainfall and catchment relief have major control on soil production.

The long term average catchment erosion rate estimated for the Bredbo catchment is 15 mm/kyr (Heimsath et al., 2001). This is comparable to the soil production rate, suggesting a stable soil resource in the catchment at these timescales. Despite the climate changes in the past (e.g. LGM) in this area, the soil mantled landscape attained stability over 30 kyr. Steady state soil weathering attained over ~10 kyr is also reported in basaltic terrains in Iceland, despite strong influence of glaciations (Vigier et al., 2006). In south-eastern Australia, however, due to increased anthropogenic activities (clearing and agriculture) since European settlement, erosion rates increased up to 245 times prior levels in south-eastern Australia (Neil and Mazari, 1993; Olley and Wasson, 2003). Increased erosion within the catchment threatens the sustainability of its soil resources.

7. Conclusions

1. Mineralogical data from weathering profiles at Frogs Hollow indicate a depth dependence of chemical weathering intensity. Muscovite content decreases with decreasing depth indicating the increased dissolution of muscovite during

644 weathering. Albite and microcline appear to be more resistant to weathering
645 than muscovite at this site.

646 2. Al_2O_3 is mobile in the soil profiles of Frogs Hollow. The Al_2O_3 concentration
647 decreases with decreasing depth. SiO_2 is comparatively immobile, as its
648 concentration increases with decreasing depth. Use of weathering indices
649 considering Al_2O_3 as immobile are not appropriate for this site, and a new Si-
650 based Weathering Index (WIS) is introduced, which shows a linear increase
651 with decreasing soil depth.

652 3. Soil evolution is very variable at the hillslope scale. Saprolite of profile F4 is
653 highly weathered and the soil formed there shows little mineralogical and
654 isotopic variation with depth. Also, saprolite of profile F1 has the lowest
655 amount of quartz, indicating a lesser extent of weathering in that saprolite than
656 in other saprolites. This saprolite has the lowest ($^{234}\text{U}/^{238}\text{U}$) and highest
657 ($^{230}\text{Th}/^{234}\text{U}$) activity ratios, probably indicating an early stage of evolution of
658 these ratios during weathering.

659 4. The relative distribution of primary minerals in the soil is not affected by
660 sequential leaching. Leached and unleached samples from profiles F1 and F2
661 do not show significant differences in mineralogy.

662 5. Soil residence times vary between 16 to 30 kyr for profile F1, and 3 to 13 kyr
663 for profile F2. The inferred soil production rates range between 15 and 24
664 mm/kyr. The calculated soil production rates are similar to previous estimates
665 determined from cosmogenic radionuclide data (Heimsath et al. 2001) and
666 corroborate that soil thickness is in steady-state at this locality.

667 6. Leached and unleached samples from profile F2 gave similar soil residence
668 timescales, though the leaching and gain coefficients of the studied nuclides
669 are different. The sequential leaching seems to significantly affect the
670 determination of leaching and gain coefficients. The removable fraction may
671 record the U-series isotope composition of the soil pore water.

672 7. Muscovite content in the soil profile shows a linear relationship with soil
673 residence time. This linear relationship provides a new method that can be
674 applied to other soil profiles to estimate soil residence timescales. Estimated
675 soil residence times of leached samples from profile F1 vary from 3 to 33 kyr,

and from 15 to 34 kyr for those from profile F3. Soil production rates for these profiles are 13 mm/kyr and 10 mm/kyr respectively.

8. The Si-based Weathering Indices of samples from soil profiles show a linear relationship with soil residence time, and hence can be used to estimate residence times of soil in profiles. For profile F3, the residence time determined vary from 20 to 28 kyr and for profile F4, they vary from 33 to 37 kyr. Soil production rates were 29 and 52 mm/kyr respectively.

9. Topographical parameters like relief and elevation appear to have significant influence on soil production rates. Higher soil production rates are observed at locations of higher relief than those at locations of lower relief. Temperature seems to have minimal impact on soil production processes. On the other hand, rainfall appears to be influential on soil production process

Acknowledgements:

We are grateful to Norman Pearson, Peter Wieland and Russell Field for assistance during sample preparation and analysis.

We thank the two reviewers for their constructive reviews and B. Marty for editorial handling of the manuscript.

POS acknowledges an iMQRES scholarship supporting this research.

AD acknowledges an ARC future fellowship FT0990447. This is Wollongong Isotope Geochronology Laboratory publication #002

HH acknowledges an ARC Linkage grant LP0990500 and an ARC future fellowship FT120100400.

The analytical data were obtained using instrumentation funded by DEST Systematic Infrastructure Grants, ARC LIEF, NCRIS, industry partners and Macquarie University.

References

- Alexander, E.B., 1988. Rates of soil formation: Implications for soil-loss tolerance. *Soil Science* 145, 37-45.
- Baeza, A., Del Rio, M., Jimenez, A., Miro, C. and Paniagua, J., 1995. Influence of geology and soil particle size on the surface-area/volume activity ratio for natural radionuclides. *Journal of Radioanalytical and Nuclear Chemistry* 189(2), 289-299.
- Chabaux, F., Blaes, E., Stille, P., di Chiara Roupert, R., Pelt, E., Dosseto, A., Ma, L., Buss, H. L., and Brantley, S. L., 2013. Regolith formation rate from U – series nuclides: Implications from the study of a spheroidal weathering profile in the Rio Icacos watershed (Puerto Rico). *Geochimica et Cosmochimica Acta* 100, 73 – 95
- Chabaux, F., Riotte, J. and Dequincey, O., 2003. U-Th-Ra fractionation during weathering and river transport, in B. Bourdon, G.M. Henderson, C.C. Lundstrom, S.P. Turner, (Eds), *Uranium-series Geochemistry, Reviews in Mineralogy and Geochemistry* 52, Geochemical Society - Mineralogical Society of America, Washington, pp. 533-576.
- Dequincey, O., Chabaux, F., Clauer, N., Sigmarsson, O., Liewig, N. and Leprun, J. C., 2002. Chemical mobilizations in laterites: Evidence from trace elements and ^{238}U - ^{234}U - ^{230}Th disequilibria. *Geochimica et Cosmochimica Acta* 66(7), 1197-1210.
- Dosseto, A., Buss, H., and Suresh, P.O., 2012. Rapid regolith formation over volcanic bedrock and implications for landscape evolution. *Earth and Planetary Science Letters* 337-338, 47-55.
- Dosseto, A., Hesse, P., Maher, K., Fryirs, K. and Turner, S. P., 2010. Climatic and vegetation control on sediment dynamics during last glacial cycle. *Geology* 38(5), 395-398.
- Dosseto, A., Turner, S. P. and Chappell, J., 2008a. The evolution of weathering profiles through time: New insights from uranium-series isotopes. *Earth and Planetary Science Letters* 274, 359-371.
- Dosseto, A., Bourdon, B. and Turner, S. P., 2008b. Uranium-series isotopes in river materials: Insights into the timescales of erosion and sediment transport. *Earth and Planetary Science Letters* 265, 1-17.
- Dosseto, A., Turner, S. P. and Douglas, G. B., 2006. Uranium-series isotopes in colloids and suspended sediments: Timescale for sediment production and transport in the Murray–Darling River system. *Earth and Planetary Science Letters* 246, 418-431.
- Driscoll, C. T., van Breemen, N., and Mulder, J. 1985. Aluminum chemistry in a forested spodosol. *Soil Science Society America Journal* 49, 437–444.

- Gleyzes, C., Tellier, S., and Astruc, M., 2002, Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures: *Trends in Analytical Chemistry* 21, 451-467.
- Hansen, R .O. and Huntington, G. L., 1969. Thorium Movements in Morainal Soils of the High Sierra, California. *Soil Science* 108(4), 257-265.
- Heimsath, A. M., Dietrich, W. E., Nishiizumi, K. and Finkel, R. C., 1999. Cosmogenic nuclides, topography, and the spatial variation of soil depth. *Geomorphology* 27, 151-172
- Heimsath, A. M., Chappell, J., Dietrich, W. E., Nishiizumi, K. and Finkel, R. C., 2000. Soil production on a retreating escarpment in southeastern Australia. *Geology* 28(9), 787-790.
- Heimsath, A. M., Chappell, J., Dietrich, W. E., Nishiizumi, K. and Finkel, R. C., 2001. Late Quaternary erosion in southeastern Australia: a field example using cosmogenic nuclides. *Quaternary International* 83-85, 169-185.
- Heimsath, A. M., Dietrich, W. E., Nishiizumi, K. and Finkel, R. C., 2001a. Stochastic processes of soil production and transport: erosion rates, topographic variation and cosmogenic nuclides in the Oregon Coast Range. *Earth Surface Processes and Landforms* 26, 531-552.
- Heimsath, A. M., Fink. D., and Hancock G. R., 2009. The 'humped' soil production function: eroding Arnhem Land, Australia. *Earth Surface Processes and Landforms* 34, 1674-1684.
- Heimsath, A. M., Chappell, J., and Fifield, K., 2010. Eroding Australia: rates and processes from Bega Valley to Arnhem Land. *Geological Society, London, Special Publications* 346, 225-241.
- Isbell, R.F., 1996, *The Australian soil classification*, CSIRO Publishing
- Kigoshi, K., 1971. Alpha-Recoil Thorium-234: Dissolution into Water and the Uranium-234/Uranium-238 Disequilibrium in Nature. *Science* 2, 47-48.
- Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42, 547-569.
- Langmuir, D. and Herman, J. S., 1980. The mobility of thorium in natural waters at low temperatures. *Geochimica et Cosmochimica Acta* 44(11), 1753-1766.
- Ma, L., Chabaux, F., Pelt, E., Blaes, E., Jin, L., and Brantley, S., 2010, Regolith production rates calculated with uranium-series isotopes at Susquehanna/Shale Hills Critical Zone Observatory. *Earth and Planetary Science Letters* 297, 211-225.

- Ma, L., Chabaux, F., West, N., Kirby, E., Jin, L., and Brantley, S., 2013, Regolith production and transport in the Susquehanna Shale Hills Critical Zone Observatory, Part 1: Insights from U – series isotopes. *Journal of Geophysical Research* 118, 1 – 19.
- Mathieu, D., Bernat, M., and Nahon, D., 1995, Short-lived U and Th isotope distribution in a tropical laterite derived from granite (Pitinga river basin, Amazonia, Brazil): Application to assessment of weathering rate. *Earth and Planetary Science Letters* 136, 703-714.
- Montgomery, D. R. 2007. Soil erosion and agricultural sustainability. *PNAS* 104(33), 13268-13272.
- Neil, D. T., and Mazari, R. K., 1993. Sediment yield mapping using small dam sedimentation surveys, southern tablelands, New South Wales. *Catena* v. 20, p. 13-25.
- Oelkers, E. H., Schott, J., Gauthier, J-M. and Herrero-Roncal, T., 2008. An experimental study of dissolution mechanism and rates of muscovite. *Geochimica et Cosmochimica Acta* 72, 4948-4961.
- Olley, J. M., and Wasson, R. J., 2003. Changes in the flux of sediments in the upper Murrumbidgee catchment, south-eastern Australia, since European settlement. *Hydrological Processes* v. 17, p. 3307- 3320.
- Owens, L.B., and Watson, J.P., 1979a, Rates of Weathering and Soil Formation on Granite in Rhodesia. *Soil Science Society of America Journal* 43, 160-166.
- Owens, L.B., and Watson, J.P., 1979b, Landscape reduction by weathering in small Rhodesian watersheds. *Geology* 7, 281-284.
- Pavich, M. J., 1989, Regolith residence time and concept of surface age of the Piedmont “Peneplain”. *Geomorphology* 2, 181-196.
- Portenga, E. W., and Bierman, P. R., 2011. Understanding Earth’s eroding surface with ¹⁰Be. *GSA Today* 21, 4-10.
- Richards, P. J., 2009. Quantification of bioturbation and its impacts on soil and slope processes, PhD Thesis, Macquarie University.
- Richardson, S. J., 1976. Geology of the Michelago 1 : 100,000 sheet 8726. Geological Survey of New South Wales, Department of Mineral Resources and Development, Canberra, Australia, 253.
- Rosenberg, P. E. and Kittrick, J. A., 1990. Muscovite dissolution at 25°C: Implications for illite/smectite-kaolinite stability relations. *Clays and Clay Minerals* 38(4), 445-447

- Rosholt, J., Doe, B. and Tatsumoto, M., (1966). Evolution of the isotopic composition of uranium and thorium in soil profiles. *Geological Society of America Bulletin* 77: 987-1004.
- Sims, K. W. W., Gill, J. B., Dosseto, A., Hoffmann, D. L., Lundstrom, C. C., Williams, R. W., Ball, L., Tollstrup, D., Turner, S., Prytulak, J., Glessner, J. J. G., Standish, J. J., and Elliott, T., 2008. An Inter-Laboratory Assessment of the Thorium Isotopic Composition of Synthetic and Rock Reference Materials. *Geostandards and Geoanalytical Research* 32(1), 65-91.
- Stillings, L. L., Drever, J. I., Brantley, S. L., Sun, Y., and Oxburgh, R., 1996. Rates of feldspar dissolution at pH 3–7 with 0–8 m M oxalic acid. *Chemical Geology* 132, 79-89.
- Suresh, P. O., Dosseto, A., Handley, H. K., and Hesse, P. P., (under revision, ARI). Assessment of a phase extraction procedure for uranium-series isotope analysis of soil and sediments.
- Troeh, F. R., Hobbs, J., and Donahue, R. L., 2004. *Soil and Water Conservation*. Prentice-Hall, Upper Saddle River, New Jersey.
- Turner, S., Calsteren, P.v., Vigier, N., and Thomas, L., 2001, Determination of thorium and uranium isotope ratios in low-concentration geological materials using a fixed multi-collector-ICP-MS: *Journal of Analytical Atomic Spectrometry* 16, 612-615.
- Turner, S., Beier, C., Niu, Y., and Cook, C., 2011. U-Th-Ra disequilibria and the extent of off-axis volcanism across the East Pacific Rise at 9°30'N, 10°30'N, and 11°20'N. *Geochem. Geophys. Geosyst.* 12, Q0AC12.
- Tyler, G. and Olsson, T., 2001. Concentrations of 60 elements in the soil solution as related to the soil acidity. *European Journal of Soil Science* 52(1), 151-165.
- Vigier, N., Bourden, B., Turner, S. and Allegre, C. J., 2001. Erosion timescales derived from U-decay series measurements in rivers. *Earth and Planetary Science Letters* 193, 549-563.
- Wakatsuki, T., and Rasyidin, A., 1992. Rates of weathering and soil formation. *Geoderma* v. 52, p. 251-263.
- White, A. F., Blum, A. E., Schulz, M. S., Bullen, T. D., Harden, J. W., and Peterson, M. L., 1996. Chemical weathering rates of a soil chronosequence on granitic alluvium: I. Quantification of mineralogical and surface area changes and calculation of primary silicate reaction rates. *Geochimica et Cosmochimica Acta* 60, 2533-2550.
- White, A. F., 2008. Quantitative approaches to characterizing natural chemical weathering rates, in Brantley, S. L., Kubicki, J. D., and White, A. F. (Eds) *Kinetics of rock water interactions*, Springer, New York, pp. 469-543.

Yoo, K., Amundson, R., Heimsath, A. M. and Dietrich, W. E., 2007. Intergration of
geochemical mass balance with sediment transport to calculate rates of soil
chemical weathering and transport on hillslopes. Journal of Geophysical
Research 112, F0 2013.

Tables

Table 1. Uranium-series isotope composition and elemental concentrations of leached and unleached soil samples from Frogs Hollow. All analytical errors are 2σ . Error associated with Tres is the standard deviation

Sample Name	Depth (cm)	Th (ppm) ^a	U (ppm) ^a	(²³⁴ U/ ²³⁸ U)	(²³⁰ Th/ ²³⁴ U)	WIS (%)
F1_Unleached						
F1aU	4±4	15.49±0.04	4.27±0.01	0.958±0.003	0.99±0.01	74.50
F1bU	12±4	15.03±0.03	5.14±0.01	0.981±0.003	0.98±0.01	71.99
F1cU	20±4	16.09±0.06	5.73±0.01	0.987±0.003	0.96±0.01	69.76
F1dU	28±4	16.92±0.05	6.53±0.01	0.997±0.003	0.95±0.01	68.47
F1eU	36±4	21.39±0.05	8.66±0.02	1.016±0.003	0.93±0.01	64.01
F1fU_sap	54±4	38.82±0.25	7.00±0.01	0.936±0.003	1.05±0.02	61.83
F2_Unleached						
F2au	4±4	22.26±0.03	6.86±0.01	0.965±0.002	0.959±0.005	
F2bu	12±4	26.48±0.05	7.87±0.02	0.978±0.003	0.92±0.01	
F2cU	20±4	26.21±0.04	9.42±0.02	0.999±0.002	0.899±0.004	70.12
F2dU_sap	34±4	30.25±0.06	11.40±0.03	1.006±0.003	0.88±0.01	65.30
F1_Leached						
F1a	4±4	9.95±0.05	3.16±0.01	0.911±0.006	0.96±0.01	
F1b	12±4	12.06±0.04	3.63±0.01	0.923±0.004	0.95±0.01	
F1c	20±4	6.52±0.02	3.56±0.01	1.024±0.005	0.93±0.01	
F1d	28±4	9.02±0.03	4.37±0.01	1.019±0.005	0.94±0.01	
F1e	36±4	12.26±0.05	6.21±0.03	1.042±0.006	0.92±0.01	
F1f_sap	54±4	33.04±0.14	6.33±0.03	0.935±0.006	1.00±0.01	
F2_Leached						
F2a	4±4	13.66±0.1	3.82±0.01	0.888±0.002	0.95±0.01	
F2b	12±4	17.08±0.04	4.98±0.01	0.913±0.002	0.96±0.01	
F2c	20±4	16.10±0.07	5.50±0.01	0.947±0.001	0.92±0.01	
F2d_sap	34±4	18.95±0.04	7.09±0.01	0.960±0.002	0.924±0.004	
F3_Leached						
F3a	4±4	11.43±0.04	2.657±0.005	0.908±0.002	0.97±0.01	77.38
F3b	12±4	13.37±0.03	2.883±0.004	0.916±0.002	0.97±0.01	74.43
F3c	20±4	12.72±0.03	3.223±0.006	0.934±0.002	0.965±0.005	73.17
F3d	28±4	12.67±0.03	3.366±0.004	0.952±0.002	0.940±0.005	71.03
F3e_sap	38±4	18.46±0.06	4.316±0.005	0.958±0.001	0.91±0.01	65.00
F4_Leached						
F4a	4±4	11.25±0.03	2.824±0.003	0.922±0.002	0.99±0.01	84.05
F4b	12±4	13.37±0.03	3.339±0.002	0.923±0.002	0.98±0.01	82.01
F4c	20±4	11.21±0.03	2.693±0.003	0.924±0.002	0.99±0.01	82.48
F4d	28±4	13.55±0.04	3.527±0.007	0.930±0.003	0.99±0.01	80.78
F4e_sap	39±4	13.65±0.03	3.348±0.007	0.930±0.003	0.97±0.01	78.91
TML3		29.41±0.01	10.527±0.022	0.994±0.003	0.994±0.008	

^a Concentrations are measured by isotope dilution.

960

961

962

Table 2. Calculated soil residence times

Sample name	Depth (cm)	Soil Residence Time (kyr)	Sample name	Depth (cm)	Soil Residence Time (kyr)	Sample name	Depth (cm)	Soil Residence Time (kyr)
Residence times determined using isotope loss-gain model (equation (1))								
F1_Unleached			F2_Unleached			F2_Leached		
F1au	4	30.3±3.6	F2au	4	10.6±5.9	F2a	4	11.8±5.9
F1bu	12	28.5±3.4	F2bu	12	13.6±4.8	F2b	12	9.1±4.8
F1cu	20	25.5±3.1	F2cu	20	2.2±1.7	F2c	20	3.2±1.8
F1du	28	24.1±2.9						
F1eu	32	15.9±1.9						
Residence times determined using muscovite content (equation (5))								
F1_Leached			F3_Leached					
F1a	4	32.9±16.4	F3a	4	33.7±16.8			
F1b	12	27.1±13.5	F3b	12	31.1±15.5			
F1c	20	24.9±12.4	F3c	20	22.0±11.0			
F1d	28	18.3±9.1	F3d	28	15.1±7.5			
F1e	32	2.9±1.4						
Residence times determined using WIS (equation (6))								
F3_Leached			F4_Leached					
F3a	4	28.5±18.6	F4a	4	37.3±19.8			
F3b	12	24.8±18.1	F4b	12	34.6±19.4			
F3c	20	23.1±17.9	F4c	20	35.2±19.5			
F3d	28	20.3±17.5	F4d	28	33.0±19.2			

963

964

965

966

967

968
969
970

Table 3. Comparison of average soil production rates with lithology, climate, seismisity and geomorphic settings

Location	Bedrock Type	Mean Elevation (m above sea level)	Mean Slope (°)	Mean Relief (m)	Average Annual Rainfall (mm)	Average Temp. (°C)	Seismicity*	Soil Production Rate (mm/kyr)	References
Pitinga Basin, Amazonia	Granitic	150	0.002	150	2000	26	2.8	50	Mathieu et al. (1995)
Tennessee valley, California	Sedimentary	220	14.4	153	920	13	3.6	45	Heimsath et al.(1999)
Nunnock River, Bega Valley	Granitic	400	9	200	910	10	0.9	43	Heimsath et al. (2000); Dosseto et al. (2008a)
Oregon Cost	Sedimentary	296	21.1	345	1748	10	2.3	150	Heimsath et al. (2001a)
Kaya, Burkino Faso	Granitic	276	2.62	100	700	10	0.0	25	Dequency et al. (2002)
Tin Can Creek (Australia)	Sedimentary	133	6.5	111	1408	27	0.7	20	Heimsath et al. (2009)
Shale Hill Observatory, Pennsylvania	Shale	290	19	30	1070	10	0.3	27	Ma et al. (2010, 2013)
Burra Creek, Canberra	Phyllite	875	8.5	25	670	13	0.9	7	Fifield et al., 2010
Bisley, Puerto Rico	Volcanoclastic	330	14.3	514	3000	22	1.9	334	Dosseto et al. (2012)
Frogs Hollow (This study)	Granitic	937	7.3	70	500	12	0.9	24	This Study

971
972

Figure Captions

Figure 1. a) Map showing the location of Frogs Hollow (FH) in the upper catchment of the Murrumbidgee River (MR). The Bredbo River (BR), the Goodradigbee River (GR) and the Tumut River (TR) are shown. Also shown is the location of the Nunnock River escarpment site (NR) previously studied by Dosseto et al. (2008a). b) Topography and curvature of the sampling site at Frogs Hollow, modified from Heimsath et al. (2001). The locations of the sampling sites (F1-F4) are shown. Soil samples were collected from the most convex points on the ridge tops to avoid laterally transported soil. c) The four soil profiles from Frogs Hollow. Soil horizon codes follow the Australian Soil Classification (Isbell, 1996). Column width is proportional to field texture: S = sand, LS = loamy sand, CS = clayey sand, GS = gravelly sand, SCL = sandy clay loam. Zig-zag lines indicate the presence of roots. Vertical black bars show sample intervals.

Figure 2. Mineral abundances (in wt. %) as a function of depth for soil profiles F1_Unleached and F1_Leached. Open circles indicate the saprolite samples.

Figure 3. (a) Uranium, (b) Thorium, (c) ($^{234}\text{U}/^{238}\text{U}$) and (d) ($^{230}\text{Th}/^{234}\text{U}$) as a function of depth in leached and unleached samples of profiles F1 and F2, and leached samples of profiles F3 and F4. All errors are of 2σ level. If not observable, errors are smaller than symbol size. Open circles represent saprolite samples.

Figure 4. Si-based Weathering Index versus depth for Frogs Hollow soil samples.

Figure 5. Soil residence times determined from the U-series model for (a) unleached samples of profile F1 and (b) leached and unleached samples of profile F2. Soil production rates are shown in the inset diagram. Open circles denote the saprolite samples.

Figure 6. (a) Soil residence time versus muscovite content (wt %) for unleached samples of soil profile F1, and leached and unleached samples of profile F2. Least square fit lines are shown. The slope of each line is given in mass %/kyr. (b) Soil production rate determined for profiles F1_Leached and F3_Leached using the muscovite contents. Open circles represent the saprolite in all figures.

Figure 7. (a) The linear relationship between WIS and residence times of soil in profile F1. The slope of this line is used to calculate residence times and production rates of soil for profiles F3 and F4. (b) Estimated soil residence time versus depth for profiles F3 and F4.

- Soil residence time from saprolite to topsoil is determined using U and Th isotope disequilibrium.
- We report notable variations in soil production rate at the small catchment scale.
- The results support steady state soil thickness in the south-eastern Australian Highlands.
- We constrain the influence of geomorphic setting on soil production rates on granitic lithology.
- Muscovite content decreases linearly and U/Th disequilibrium increases with soil residence time.

Figure 1
[Click here to download high resolution image](#)

Figure 2
[Click here to download high resolution image](#)

Figure 3
[Click here to download high resolution image](#)

Figure 4
[Click here to download high resolution image](#)

Figure 5
[Click here to download high resolution image](#)

Figure 6
[Click here to download high resolution image](#)

Figure 7
[Click here to download high resolution image](#)

Analytical Techniques

All soil samples were first dry-sieved at 500 μm and then wet sieved at 53 μm . The < 53 μm fractions were collected in aluminum trays and dried at 60°C. The < 53 μm size fraction was selected for geochemical and isotopic study as it is expected to have higher concentrations of radioactive elements compared to larger grain size fractions (Baeza et al., 1995). Moreover, the depletion of ^{234}U , as a result of alpha recoil, is expected to be measurable only in mineral grains smaller than about 50 μm (DePaolo et al., 2006). Previous studies on the U-series isotope composition of soils have largely focused on bulk sample material. However, soil is a complex mixture of organic material, primary and secondary minerals. In order to assess the effect of organic matter and secondary phases on the U-series isotope composition of soils, we analyzed (i) the < 53 μm size fraction of bulk soil samples (hereafter referred as “unleached”) and (ii) the 2-53 μm size fraction of soil samples after sequential leaching (referred to as “leached”). Sequential leaching was carried out in order to remove organic compounds and secondary mineral phases, leaving only the residual primary minerals from the bedrock. The sequential leaching procedure used here is modified from that of Schultz et al. (1998) and is detailed in Table A.1 of the supplementary material. An additional step has been added for the removal of clays by centrifugation. Note that clays mentioned here refer to their granulometrical definition only, not mineralogical, i.e. the size fraction < 2 μm , which may contain other mineral phases besides clay. The leaching procedure has been tested using powdered TML – 3 (Table Mountain Latite) and BCR – 2 (Columbia River Basalt) standards which have U-series activity ratios in secular equilibrium (Williams et al., 1992; Turner et al., 2001; Hoffman et al., 2007; Sims et al., 2008; Prytulak et al., 2008), to assess whether any isotopic fractionation is introduced during the leaching process. The ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) ratios of the unleached and leached TML – 3 and BCR – 2 aliquots were found (Suresh et al., in prep) to be within the measured 2 σ precision limits (8 ‰ for ($^{234}\text{U}/^{238}\text{U}$) and 2 % for ($^{230}\text{Th}/^{238}\text{U}$)) (Sims et al., 2007, Turner et al., 2011), indicating that the sequential leaching procedure does not introduce any artifact to the U-series activity ratios of samples. The mineralogy of leached and unleached aliquots was determined by X-ray diffraction (XRD). The Rietveld refinement method in the HighScore Plus software from PANalytical was used to quantify mineral abundances. Particle size distribution was determined using a Micromeritics Sedigraph particle analyzer at Macquarie University.

Unleached samples for major element analysis were powdered below 10 μm using agate mortar and pestle and made into 40 mm glass discs by fusion with lithium borate containing lanthanum oxide, following the procedure described by Norrish and Hutton (1969). Samples were analyzed on a Philips PW2400 XRF instrument at the Mark Wainwright Analytical Centre of

University of New South Wales. Replicate analyses were performed to determine reproducibility and the standard error for SiO₂ measurements of 3 replicate of a sample was 0.07 %.

All samples were spiked with a ²³⁶U-²²⁹Th tracer and then digested using a mixture of HCl, HNO₃, HF and HClO₄. Uranium and thorium were separated and purified using an anion exchange resin (Biorad AG1X8) as described in Sims et al. (2008) and Dosseto et al. (2006). The purified U and Th fractions were analyzed on a Nu Instruments Nu34 multi-collector ICP-MS at Macquarie University following the procedure described in Turner et al. (2011) and Sims et al. (2008). External analytical uncertainties were determined by replicating multiple aliquot analyses of leached and unleached samples (all errors are 2σ). For the leached sample replicates, Th concentration varies by 7 to 25%, and U content by 7%. The (²³⁴U/²³⁸U) ratio of leached aliquots varies by 1 to 5% and their (²³⁰Th/²³⁴U) ratio varies by 1 to 2%. For unleached sample replicates, Th concentration varies by 5 to 20%, and U content by 1 to 2%. The (²³⁴U/²³⁸U) ratio of leached aliquots varies by 0.5 to 1% and their (²³⁰Th/²³⁴U) by 0.7%. The (²³⁴U/²³⁸U) and (²³⁰Th/²³⁴U) ratios are more reproducible in unleached aliquots compared to leached aliquots. The lower reproducibility of leached aliquots could be due to readsorption of isotopes back to the residue of leaching, although this has not been tested. Accuracy was determined by analyzing the TML-3 rock standard and measured values are within published values by 1.1% for Th concentration, 0.06% for U concentration, and 0.6% for (²³⁴U/²³⁸U) and (²³⁰Th/²³⁴U) ratios (Table 1). Total procedural blanks were typically 70 pg for Th and 20 pg for U.

Table A.1. Sequential leaching procedure, modified from Schultz et al. (1998)

Leached fraction	Reagents	Process
1) Exchangeable/adsorbed/organics	Sodium hypochlorite at pH 7.5 adjusted with HCl (15ml/g of sample)	Keep the sample in the oven at 98°C for 30 minutes Centrifuge at 7000 rpm for 15 minutes and discard supernatant. Repeat these steps, add 10 ml ultra-pure water and centrifuge to rinse
2) Carbonates	1 M sodium acetate, adjusted to pH 4 with acetic acid (10ml/g of sample)	Agitate at room temperature for 2 hours, centrifuge at 7000 rpm for 15 minutes and discard supernatant. Repeat these steps and then add 10 ml ultra-pure water and centrifuge to rinse
3) Amorphous and crystalline Fe-Mn oxides	0.04 M hydroxylamine hydrochloride	Agitate at room temperature for 5 hours, centrifuge at 7000 rpm for 15 minutes, discard supernatant, add 10 ml Milli-Q water and centrifuge to rinse
4) Clay	5% sodium hexa meta phosphate solution, 50ml	Ultrasonicate with 190 W power for 20 s, agitate overnight, centrifuge at 1500 rpm for 34 seconds discard supernatant, and repeat centrifuging with Milli-Q water until supernatant is clear

Table A.2. Mineralogical data of soil samples from Frogs Hollow

Sample Name	Quartz (%)	Albite (%)	Muscovite (%)	Microcline (%)
F1_Leached				
F1a	43.5	40.3	0	16.2
F1b	37.9	39.1	4.8	18.1
F1c	38.9	40.4	6.7	13.9
F1d	31.9	42.6	12.2	13.3
F1e	19.4	42.3	25.1	12.6
F1f_sap	10.1	49.1	27.6	13.2
F2_Leached				
F2a	50.4	19.9	10.2	19.5
F2b	51.5	24.4	4.2	19.9
F2c	45.6	23.4	15.1	15.9
F2d_sap	45	15.3	17.6	22.1
F3_Leached				
F3a	57.4	29.4	0	13.2
F3b	53.2	30.2	2.2	14.4
F3c	59.7	30.6	9.8	0
F3d	43.1	28.5	15.6	12.8
F3e_sap	27.9	28.3	28.3	15.4
F4_Leached				
F4a	71.8	14.5	0	13.6
F4b	72.6	15.3	0	12.1
F4c	69.3	17	0	13.7
F4d	73.3	14	0	12.7
F4e_sap	70.3	15.4	1.7	12.6
F1_Unleached				
F1aU	39.7	44.4	0	15.9
F1bU	34.8	40.2	8.2	16.7
F1cU	34	44.7	9.7	11.6
F1dU	34.4	39.7	14.2	11.7
F1eU	24.7	41.4	23.2	10.7
F1fU_sap	14.1	44.8	31	10.1
F2_Unleached				

F2au	53.9	23	4.7	18.4
F2bu	49.5	23.6	7.1	19.7
F2cU	42.7	24.3	13.8	19.2
F2dU_sap	41.9	15.9	15.2	27

Concentrations are given as mass percentage

Table A. 3. Major element data of soil samples from Frogs Hollow

Elemental oxide	F1a	F1b	F1c	F1d	F1e	F1f_sap	F2c	F2d_sap	F3a	F3b	F3c	F3d	F3e_sap	F4a	F4b	F4c	F4d	F4e_sap
SiO ₂ (%)	62.91	61.63	59.76	57.45	50.78	47.96	55.9	49.42	66.67	63.53	62.11	58.58	51.05	74.22	71.41	72.46	70.39	67.09
TiO ₂ (%)	0.54	0.66	0.74	0.79	1.05	0.88	0.99	1.07	0.61	0.71	0.77	0.81	0.9	0.83	1	0.95	1.13	1.13
Al ₂ O ₃ (%)	15.65	17.72	20.12	21.13	24.61	26.36	20.52	24.47	14.25	16.51	17.69	19.26	24.24	10.66	12.26	11.98	13.6	15.22
Fe ₂ O ₃ (%)	3.19	3.64	4.23	4.94	6.19	6.98	5.7	7.31	3.26	3.76	4.17	4.87	6.38	2.55	2.85	2.8	3.33	4.03
Mn ₃ O ₄ (%)	0.14	0.09	0.07	0.07	0.06	0.06	0.08	0.07	0.15	0.12	0.09	0.07	0.07	0.07	0.06	0.05	0.05	0.05
MgO (%)	0.39	0.43	0.53	0.66	0.96	1.01	0.89	1.21	0.39	0.46	0.53	0.69	1.06	0.26	0.27	0.28	0.37	0.53
CaO (%)	2.88	3.07	2.76	2.6	1.81	1.26	1.9	1.05	3.04	3.12	3.01	2.75	1.89	1.87	1.78	1.78	1.64	1.43
Na ₂ O (%)	3	3.19	3.02	2.72	2.13	1.99	1.4	0.74	2.2	2.19	2.08	1.88	1.36	1.55	1.62	1.63	1.51	1.28
K ₂ O (%)	2.67	2.75	2.93	2.94	3.07	2.67	3.17	2.99	2.7	2.88	2.99	2.99	3	2.74	2.96	2.93	3.18	3.26
P ₂ O ₅ (%)	0.09	0.04	0.04	0.04	0.06	0.06	0.06	0.08	0.07	0.07	0.05	0.04	0.06	0.05	0.05	0.04	0.04	0.04
SO ₃ (%)	0.07	0.05	0.04	0.03	0.03	BLD	0.03	0.02	0.05	0.05	0.01	0.03	0.01	0.06	0.02	0.04	0.05	0.04
Cr ₂ O ₃ (%)	BLD*	BLD	0.01	BLD	0.01	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	0.01	BLD	0.01	0.01
ZrO ₂ (%)	0.11	0.1	0.07	0.07	0.04	0.04	0.09	0.05	0.13	0.11	0.12	0.1	0.05	0.13	0.11	0.11	0.1	0.08
SrO (%)	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.01	0.02	0.01
ZnO (%)	0.01	BLD	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	BLD	BLD	BLD	0.01	0.01
NiO (%)	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD
BaO (%)	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.06	0.05
PbO (%)	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD	BLD

*BLD = Below the Limit of Detection

Table A.4. Median particle size and clay to silt ratio of unleached soil samples from Frogs Hollow

Sample name	Median particle size (μm)	Clay to silt ratio
F1a	22.2	0.022
F1b	15.6	0.111
F1c	12.1	0.088
F1d	14.8	0.092
F1e	10.6	0.096
F1f_sap	11.6	0.112
F2a	14.2	0.084
F2b	11.4	0.127
F2c	10.3	0.125
F2d_sap	8.0	0.225
F3a	15.5	0.097
F3b	13.1	0.091
F3c	14.5	0.094
F3d	11.8	0.093
F3e_sap	10.0	0.161
F4a	17.3	0.062
F4b	12.8	0.077
F4c	15.4	0.046
F4d	12.3	0.097
F4e_sap	11.4	0.104

Table A.5. Leaching and input coefficients inferred from the nuclide loss/gain model.

Profile	k_{238} ($\times 10^{-5} \text{ yr}^{-1}$)	k_{234} ($\times 10^{-5} \text{ yr}^{-1}$)	k_{230} ($\times 10^{-5} \text{ yr}^{-1}$)	f_{238} ($\times 10^{-5} \text{ yr}^{-1}$)	f_{234} ($\times 10^{-5} \text{ yr}^{-1}$)	f_{230} ($\times 10^{-5} \text{ yr}^{-1}$)
F1_Unleached	1.8 $\pm$ 0.2	6.2 $\pm$ 3.9	3.6 $\pm$ 0.4	1.0 $\pm$ 0.1	0.7 $\pm$ 0.4	1.3 $\pm$ 0.1
F2_Unleached	3.0 $\pm$ 0.1	8.4 $\pm$ 0.1	17.9 $\pm$ 0.2	0.7 $\pm$ 0.003	5.2 $\pm$ 1.4	1.2 $\pm$ 0.001 $\times 10^{-8}$
F2_Leached	0.4 $\pm$ 0.1	1.3 $\pm$ 0.6	1.1 $\pm$ 0.65 $\times 10^{-5}$	3.6 $\pm$ 3.0	1.5 $\pm$ 0.2	6.8 $\pm$ 3.8

Table A.6. Upper limits of soil mixing rate

Profile	Soil mixing rate (g/m ² /year)
F1_Unleached	16.5±5.5
F1_Leached	14.3±2.3
F2_Unleached	26.4±5.5
F2_Leached	19.8±8.8
F3_Leached	11.1±1.1

Fig. A.1. Mineral abundances (in wt. %) as a function of depth for soil profiles: (a) F1_Unleached and F1_Leached, (b) F2_Unleached and F2_Leached, (c) F3_Leached and (d) F4_Leached. Open circles indicate the saprolite samples.

Fig. A.2. U/Th ratios (normalized to the corresponding underlying saprolites) versus depth for Frogs Hollow soil samples.

Fig. A.3. Comparison of (a) Uranium, (b) Thorium, (c) $^{234}\text{U}/^{238}\text{U}$ and (d) $^{230}\text{Th}/^{234}\text{U}$ of leached and unleached aliquots of samples from soil profiles F1 and F2.

Fig. A.4. Relationship between soil production rate and catchment relief or average annual rainfall. (Data from Table 4)

References

- Baeza, A., Del Rio, M., Jimenez, A., Miro, C. and Paniagua, J., 1995. Influence of geology and soil particle size on the surface-area/volume activity ratio for natural radionuclides. *Journal of Radioanalytical and Nuclear Chemistry* 189(2), 289-299.
- DePaolo, D. J., Maher, K., Christense, J. N. and McManus, J., 2006. Sediment residence time measured with U-series isotopes: Results from ODP North Atlantic drift site 984. *Earth and Planetary Science Letters* 248(1-2), 394-410.
- Hoffmann, D. L., Prytulak, J., Richards, D. A., Elliott, T., Coath, C. D., Smart, P. L. and Scholz, D., 2007. Procedures for accurate U and Th isotope measurements by high precision MC-ICPMS. *International Journal of Mass Spectrometry* 264, 97-109.
- Norrish, K., and Hutton, J. T., 1969. An accurate spectrographic method for the analysis of a wide range of geological samples. *Geochimica et Cosmochimica Acta* 33, 431-451.
- Prytulak, J., Elliott, T., Hoffmann, D.L., and Coath, C.D., 2008, Assessment of USGS BCR-2 as a Reference Material for Silicate Rock U-Pa Disequilibrium Measurements: *Geostandards and Geoanalytical Research*, v. 32, p. 55-63.
- Schultz, M. K., Burnetta, W. C. and Inn, K. G. W., 1998. Evaluation of a Sequential Extraction Method for Determining Actinide Fractionation in Soils and Sediments. *Journal of Environmental Radioactivity* 40(2), 155-174.

- Sims, K. W. W., Gill, J. B., Dosseto, A., Hoffmann, D. L., Lundstrom, C. C., Williams, R. W., Ball, L., Tollstrup, D., Turner, S., Prytulak, J., Glessner, J. J. G., Standish, J. J., and Elliott, T., 2008. An Inter-Laboratory Assessment of the Thorium Isotopic Composition of Synthetic and Rock Reference Materials. *Geostandards and Geoanalytical Research* 32(1), 65-91.
- Suresh, P. O., Dosseto, A., Handley, H. K., and Hesse, P. P., (under revision, ARI.). Assessment of a phase extraction procedure for uranium-series isotope analysis of soil and sediments.
- Turner, S., Calsteren, P.V., Vigier, N., and Thomas, L., 2001, Determination of thorium and uranium isotope ratios in low-concentration geological materials using a fixed multi-collector-ICP-MS: *Journal of Analytical Atomic Spectrometry* 16, 612-615.
- Williams, R.W., Collerson, K.D., Gill, J.B., and Deniel, C., 1992, High Th/U ratios in subcontinental lithospheric mantle: mass spectrometric measurement of Th isotopes in Gaussberg lamproites: *Earth and Planetary Science Letters* 111, 257-268.