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Abstract

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Disciplines

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Chemical Weathering (U-Series)

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Synonyms (if applicable)

Regolith formation rates; Soil formation rates

Definition

Uranium-series (U-series) isotopes are radionuclides that compose the ^{238}U and ^{235}U decay chains.

Measurements of U-series isotopes in soils and river sediments can be used to infer timescales of chemical weathering, and derive quantitative estimates of soil age and production rates as well as sediment transport rates through catchments.

Main text

Historical material

U-series isotopes in geological materials have received significant interest since the 1960's (Adams et al. 1959, Pliler and Adams 1962, Cherdyntsev et al. 1964, Rosholt et al. 1966, Syromyatnikov et al. 1967, Hansen and Stout 1968, Scott 1968, Syromyatnikov and Ivanova 1968, Cherdyntsev 1971, Titayeva and Veksler 1977) or even earlier, when investigations were mostly supported by governmental programs motivated by the development of raw materials for nuclear weapons and power (Adams et al. 1959). The first studies were interested with the mobility of actinides in weathering profiles (Pliler and Adams 1962, Rosholt et al. 1966, Hansen and Stout 1968, Hansen and Huntington 1969, Moreira-Nordemann 1977, Moreira-Nordemann 1980) while others were investigating the radioactive disequilibrium associated with uranium ore deposits (Cherdyntsev et al. 1964, Syromyatnikov et al. 1967, Lively et al. 1979), in groundwaters (Osmond and Cowart 1976, Cowart and Osmond 1977, Krishnaswami et al. 1982, Osmond and Cowart 1982, Osmond et al. 1983) or in streams and estuaries (Scott 1968, Martin et al. 1978, Mangini et al. 1979). Early studies in nuclear physics examined the mechanisms for U-series isotope fractionation (e.g. Linhard and Scharff 1961,

Harvey 1962). Later work would explore how these processes could account for radioactive disequilibrium in geological materials with a focus on recoil and preferential leaching effects (Kigoshi 1971, Fleischer and Raabe 1978b, Fleischer and Raabe 1978a, Fleischer 1980, Fleischer 1982a, Fleischer 1982b, Fleischer 1983, Sheng and Kuroda 1984, Hussain and Lal 1986, Dran et al. 1988, Adloff and Roessler 1991). Despite a large body of early work on U-series isotope fractionation during chemical weathering, the 1980's and 1990's saw a decrease in interest for this application. However, the topic has regained interest since the late 1990's and early 2000's, in part thanks to improved chemical separation methods (Horwitz et al. 1993, Chabaux et al. 1994, Horwitz 1996, Bourdon et al. 1999) and the development of plasma source mass spectrometry allowing the precise measurement of low abundance U-series isotopes (e.g. Turner et al. 2001).

Essential concepts and applications in more detail

Uranium-238 (^{238}U) decays through a series of radioactive products to ^{206}Pb as the final, stable isotopic product (Figure 1). The ^{238}U decay chain is composed of a series of daughter-parent systems where each daughter nuclide is the result of alpha or beta disintegration of the parent nuclide. Although “uranium-series” refer to both ^{238}U and ^{235}U decay chains, most studies focus on the decay products in the ^{238}U decay series, in particular three isotopes: ^{238}U , the parent nuclide of the decay series; ^{234}U , which is produced after alpha decay of ^{238}U into ^{234}Th followed by rapid decays to ^{234}Pa (by beta emission (of ^{234}Th with a half-life of 24.1 days), and ^{234}U (by beta emission of ^{234}Pa with a half-life of 6.67 hours); and ^{230}Th , produced by alpha decay of ^{234}U with a half-life of 2.46×10^5 a).

For any geological system that remains closed to mass exchange for more than a million years, all radioactive systems in the decay chain are in *secular equilibrium*, i.e. the activity of the daughter nuclide equals that of the parent. The *activity* of a nuclide is its rate of decay, i.e. the product between its abundance and its decay constant. Results are generally expressed in term of daughter to parent activity ratios, for instance ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$), with the use of parentheses indicating activities. Thus, if a system is in secular equilibrium, these ratios are equal to unity.

A variety of geological processes induce fractionation between U-series isotopes, termed *radioactive disequilibrium*, in which case the activity ratio deviates from unity. Once a disequilibrium is produced, the parent-daughter system will tend to return to secular equilibrium via radioactive decay, over a timescale that is about five times the half-life of the daughter nuclide (for instance, 1.2 Ma for ^{238}U - ^{234}U ; 375 ka for ^{234}U - ^{230}Th). Thus, the value of the activity ratio in a geological sample is a function of (i) the behaviour of isotopes during geological processes and (ii) the time elapsed since fractionation for a discrete process, or the rate of fractionation for a continuous process.

a. Mechanisms of U-series disequilibrium

Uranium can be found in two stable oxidation states: 4 and 6, while the only stable oxidation state for thorium is tetravalent. At low oxygen fugacity (i.e. reducing conditions as it is common in the Earth's

interior), uranium is tetravalent and has properties similar to thorium, although differences exist which yield ^{230}Th - ^{238}U disequilibrium in magmas (Harmon and Rosholt 1982, Bourdon et al. 2003, Lundstrom 2003, Turner et al. 2003b, Dosseto et al. 2010). Under oxidizing conditions (as it is commonly the case at the Earth's surface), U is present in its hexavalent state and forms the uranyl ion UO_2^{2+} . This ion can form stable carbonyl complexes, which accounts for uranium's solubility in natural waters. In contrast, thorium is relatively insoluble at pH values typical of surface waters (5-8) and it is soluble only in the presence of organic acids at low pH (<3), via binding to organic colloids (Langmuir and Herman 1980, Viers et al. 1997). As a consequence of these chemical behaviours, solutes (e.g. groundwaters, soil pore waters, and stream waters) are generally enriched in U relative to Th and are characterized by $(^{230}\text{Th}/^{238}\text{U})$ activity ratios less than 1. *Weathering products* (hereby restricted to *solid* weathering products, i.e. weathered rocks, soils, stream sediments) are generally enriched in Th relative to U and show $(^{230}\text{Th}/^{238}\text{U})$ activity ratios greater than 1 (Syromyatnikov and Ivanova 1968, Titayeva and Veksler 1977, Latham and Schwarcz 1987).

Although ^{234}U and ^{238}U theoretically have the same chemical behaviour, as illustrated by the absence of significant fractionation in igneous rocks, fractionation between these two isotopes occurs at the Earth's surface, resulting in an enrichment of ^{234}U in natural waters and a depletion in weathered rocks, soils and sediments (Syromyatnikov and Ivanova 1968, Titayeva and Veksler 1977, Latham and Schwarcz 1987). This fractionation occurs as a consequence of two processes: (i) direct recoil of ^{234}Th out of the mineral grain during alpha decay of ^{238}U and subsequent beta decays into its granddaughter ^{234}U (Figure 1; Kigoshi 1971). This occurs because when ^{238}U decays into ^{234}Th , the daughter is displaced by 15-35 nm (the *recoil length*) in most minerals (Hashimoto et al. 1985). If this occurs within a recoil length from the mineral surface, a fraction of ^{234}Th can be lost to the surrounding medium (air or water; Figure 2 case (a1)). (ii) Preferential leaching of ^{234}U embedded in recoil tracks (Fleischer 1980, Fleischer 1982b). The fraction of recoiled ^{234}Th that is not directly ejected into the surrounding medium is embedded in recoil tracks either deeper the source mineral (Figure 2 case (a2)), or into adjacent minerals (Figure 2 case (a3)) especially when the pore space is filled with air (Sun and Furbish 1995). When a solution fills the pore space, the ^{234}U produced by decay is leached out of the exposed recoil tracks in adjacent minerals (Figure 2 case (b3)) (Fleischer 1980, Andersen et al. 2009), or from newly exposed recoil tracks as a result of dissolution of the source mineral (Figure 2 case (b2)). Complete leaching of embedded nuclides occurs over a timescale as short as 200 years (Fleischer 1980).

Initially, it was proposed that by determining the fraction of ^{234}Th directly recoiled out of minerals one could quantify the supply rate of ^{234}U to the solution leaching these minerals (Kigoshi 1971). However, it was later postulated that preferential leaching of embedded ^{234}U is another important mechanism for the delivery of ^{234}U to solutions (Fleischer 1980). It is important to note that although differentiating both

mechanisms is important to accurately study the enrichment of solutions in ^{234}U over ^{238}U , when studying the complementary depletion in ^{234}U in residual solids (as it is the case below), such differentiation is not necessary. Indeed, assessments of recoiled ^{234}Th can over-estimate the actual amount of ^{234}U lost to the solution if a significant proportion is embedded into adjacent grains; however, it is exactly because these embedded nuclides are subsequently leached from recoil tracks that eventually all recoiled ^{234}Th end up being lost from the minerals (whether directly recoiled in the water or embedded to another grain and later leached).

As mentioned above, radioactive disequilibrium is generally reported as the ratio of daughter to parent activity, e.g. ($^{234}\text{U}/^{238}\text{U}$). The activity ratios used to report U-Th disequilibrium in the literature vary: some studies report ($^{230}\text{Th}/^{234}\text{U}$) while others use ($^{230}\text{Th}/^{238}\text{U}$). Since ^{230}Th is the produce of ^{234}U decay, it could seem more sensible to report ($^{230}\text{Th}/^{234}\text{U}$) ratios. However, if the aim is to study the U-Th disequilibrium imparted by the difference in mobility of U and Th during mineral dissolution, this ratio may not be appropriate: ^{234}U is not only sensitive to U mobilization during dissolution but also to direct recoil and preferential leaching of ^{234}U embedded in recoil tracks. ^{230}Th is also sensitive to these two processes but because of the high reactivity of Th with particle surfaces, it is highly likely that the ^{230}Th released by recoil or preferential leaching will rapidly re-adsorb on mineral grains. As a consequence, the ($^{230}\text{Th}/^{238}\text{U}$) activity ratio may be a more appropriate measure of the U-Th disequilibrium that occurs during mineral dissolution.

b. Occurrence of U-series nuclides in weathering products

Weathering products can be simplified as the mixture of four components: (i) primary minerals (i.e. mineral phases from the parent rock), (ii) secondary minerals produced during incongruent dissolution of primary minerals, (iii) secondary minerals produced by precipitation from soil pore water and (iv) organic matter. Our understanding of the occurrence of U-series disequilibrium is bound to the distribution of U in these components.

As reviewed in Chabaux et al. (2003), uranium can be sorbed onto mineral surfaces with a sorption efficiency ranked as follows: Fe oxides and silica gels > clays and micas > opals (Ames et al. 1983a). For Fe oxides, the sorption efficiency is ordered as follows: amorphous Fe-oxyhydroxides > goethite > hematite (Ames et al. 1983a, Ames et al. 1983c, Hsi and Langmuir 1985, Manceau et al. 1992, Waite et al. 1994). For clays, U sorption efficiency is in the following order: montmorillonite > illite > kaolinite (Borovec 1981, Ames et al. 1983a, Shirvington 1983). U can also be sorbed on micas, mostly on muscovite, with a low sorption efficiency for biotite and phlogopite (Ames et al. 1983b). Near-neutral pH conditions tend to favour U sorption, while in acidic conditions, U sorption is enhanced by the presence of humic acids (Lenhart and Honeyman 1999). It has been shown that in some cases, organic acids can control the U budget of weathering products (Plater et al. 1992, Porcelli et al. 1997, Andersson et al. 1998, Dequincey et al. 2002,

Chabaux et al. 2003, Vigier et al. 2005, Dosseto et al. 2006a, Dosseto et al. 2006b). Plater et al. (1992) showed that, for bedload sediments from the Witham River in the U.K., the organic fraction accounts for 2-12 wt. % of the total U budget, while amorphous and crystalline Fe-Mn oxyhydroxides represent 10-20 wt. %. They found that resistate minerals, i.e. primary minerals, concentrate 62-85 wt. % of the U in the sediments.

In primary minerals, U is mostly found in accessory phases with zircon, xenotime or monazite exhibiting concentrations as high as several 1000's of ppm, while ilmenite and magnetite have U concentrations between a few ppm and several 10's of ppm, and apatite between 5 and 150 ppm (Adams et al. 1959). Major minerals like quartz or feldspars contain sub-ppm to ppm levels of U, most likely in liquid inclusions or submicroscopic inclusions of accessory minerals (Adams et al. 1959). Other major minerals like micas or amphiboles can contain up to 10's of ppm of U. Interstitial U, i.e. at grain boundaries, along cleavages and in microfractures, is another significant pool of uranium in igneous parent rocks (Tieh and Ledger 1981, Guthrie and Kleeman 1986). Guthrie and Kleeman (1986) showed that during the early stages of granite weathering, "background" U (i.e. contained in quartz and feldspars) is re-distributed to the interstitial pool, and a net loss of U occurs via (i) decrease of the interstitial U pool and (ii) dissolution of accessory minerals. While the modal abundance of these accessory minerals decreases, their U concentration remains constant.

As shown below, U-series disequilibrium has been used in weathering products to determine the time elapsed since conversion of the parent rock into soils and sediments. In this respect, it is important to note the behaviour of primary minerals during weathering is as important as their U content: to impart radioactive disequilibrium to the weathering product, a mineral must not only (i) contain a significant amount of U but must also (ii) actively dissolve yet (iii) survive chemical weathering. On the one hand, for a U-rich mineral like zircon, because it is highly resistant to chemical weathering, it is likely that no significant loss of nuclides occur via dissolution (Figure 3). However, it has been shown that intense metamictization can favour zircon weatherability (Balan et al. 2001). Note also that recoil can implant significant amounts of ^{234}U and ^{230}Th to adjacent minerals that may actively dissolve and this can result in a net loss of these nuclides. On the other hand, a U-rich mineral that readily dissolves and is consumed early during weathering will have no contribution to the ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) ratios of the weathering product since all its U-series nuclides will have been lost to the solution (Figure 3). Thus, the U-series isotope composition of primary minerals and their products is controlled by the U-rich minerals that actively dissolve but survive the weathering process (Figure 3). This was recently confirmed by a study of soil profiles in south-eastern Australia which found a correlation between the soil residence time inferred from U-series isotopes and the soil muscovite content (Suresh et al. 2011, Suresh et al. 2013).

c. Models of U-series disequilibrium in weathering products

The time-sensitive property of U-series isotopes offers the perspective of being able to determine time constraints on weathering processes. Early studies investigated the qualitative potential of mechanisms to account for observed U-series isotope compositions in soils (e.g. Rosholt et al. 1966, Rosholt 1982). Latham and Schwarcz (1987) and Scott et al. (1992) later developed quantitative models that would describe the evolution of nuclide abundances in weathering products.

In Latham and Schwarcz (1987), a uranium-leach model was proposed to account for $(^{234}\text{U}/^{238}\text{U}) \leq 1$ and $(^{230}\text{Th}/^{238}\text{U}) > 1$ in weathered granitic rocks. In this model, the abundance of a daughter nuclide, d , in the solid (rock, soil, or sediment) varies with time as a function of the amount of nuclides gained by radioactive decay of the parent, p , and the amount lost by their own decay and via dissolution:

$$\frac{dN_d}{dt} = \lambda_p \cdot N_p - \lambda_d \cdot N_d - w_d \cdot N_d \quad (1)$$

where N_p and N_d are the number of atoms of the parent and daughter nuclides, respectively, λ_p and λ_d are the decay constants for the parent and daughter nuclides, respectively (in a^{-1}), and w_d is a coefficient that represents the combined loss of the daughter nuclide during mineral dissolution and as a result of recoil when applicable (in a^{-1}). For ^{238}U , the first two terms on the right hand side are absent because there is no parent and ^{238}U decay can be neglected over the timescales considered (< 1 Ma).

Scott et al. (1992) proposed a similar weathering model that also explicitly accounts for the loss via recoil of a daughter nuclide produced by α decay.

$$\frac{dN_d}{dt} = (1 - f_d) \lambda_p \cdot N_p - \lambda_d \cdot N_d - w'_d \cdot N_d \quad (2)$$

where f_d is the fraction of daughter nuclide lost by recoil. In this formulation, w'_d is a coefficient that accounts for the loss of daughter nuclide via mineral dissolution only, i.e., if $f_d > 0$, $w'_d < w_d$. Note that for non-radiogenic nuclides (e.g., ^{238}U) or nuclides produced by β decay (e.g., ^{231}Pa), $w' = w$. While ^{234}U is produced by β decay from ^{234}Pa , it is lost by α recoil of ^{234}Th which rapidly decays into ^{234}Pa (half-life, $T_{234\text{Th}} = 24.1$ days), which rapidly decays into ^{234}U ($T_{234\text{Pa}} = 6.09$ hours).

It has been proposed that in silt-sized sediments ^{234}U - ^{238}U fractionation occurs mainly via recoil and loss of ^{234}U to the surrounding medium (Maher et al. 2004, DePaolo et al. 2006). In this case, it is assumed that

$w'_4 = w'_8$ and equation (2) can be re-arranged to express the ($^{234}\text{U}/^{238}\text{U}$) of the sediment as a function of time:

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) = \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_0 \cdot e^{-\lambda_4 t} + (1 - f_4)(1 - e^{-\lambda_4 T_{comm}}) \quad (3)$$

where ($^{234}\text{U}/^{238}\text{U}$)₀ is the initial activity ratio. T_{comm} is termed the comminution age, and represents the amount of time needed for the activity ratio to evolve from its initial value (generally the source rock in secular equilibrium) to the observed value in the sediment. Note that because this approach neglects the effect of chemical weathering (mineral dissolution) on U-series isotope fractionation, it is not discussed further in this contribution. The reader is referred to DePaolo et al. (2012) for a recent review.

Dequincey et al. (1999, 2002) proposed a model that allows not only for the loss of nuclide via mineral dissolution but also for its gain via precipitation of secondary minerals or dust deposition. For instance, the evolution of the abundance of a radiogenic nuclide in the solid is predicted by the equation:

$$\frac{dN_d}{dt} = \lambda_p \cdot N_p - \lambda_d \cdot N_d + \frac{F_d}{\lambda_d} - w_d \cdot N_d \quad (4)$$

where F_d is the activity input of the daughter nuclide per time unit (in atoms/a²). Note that here, recoil is not explicitly accounted for and is lumped into the dissolution coefficient, as in Latham and Schwarcz (1987).

Dosseto et al. (2008b) later modified this expression and introduced an input coefficient, Γ (in a⁻¹), such that input and dissolution coefficients could be directly compared.

$$\frac{dN_d}{dt} = \lambda_p \cdot N_p - \lambda_d \cdot N_d + \Gamma_d N_{d,i} - w_d \cdot N_d \quad (5)$$

The input coefficient Γ_d reflects how fast the initial concentration $N_{d,i}$ is increased by nuclide addition. Thus, the term $\Gamma_d N_{d,i}$ represents the flux of added nuclides (in atoms/g/a). Note that the model is sensitive to the initial isotopic ratios but not to the initial isotopic abundances (i.e. the initial U concentration, $N_{d,i}$, does not impact calculated activity ratios, but the initial activity ratios obviously do).

In order to better understand the evolution of each nuclide's abundance in the solid according to these models, processes that affect the mobility of each nuclide are reviewed below.

Mobility of ^{238}U :

- Loss during mineral dissolution, releasing ^{238}U to the solution (coefficient w_8). The ability of ^{238}U to stay in solution then depends of the redox conditions, as explained above: in reducing conditions, tetravalent ^{238}U has low solubility and will precipitate out of the solution, while in oxidising conditions (typical of near-surface environments where mineral dissolution by weathering takes place), ^{238}U will form the uranyl ion $^{238}\text{UO}_2^{2+}$ which readily complexes with the carbonate ion to create a very stable and highly soluble species.
- Sorption from soil pore water onto mineral surfaces (coefficient Γ_8). It has been shown that uranium can be easily adsorbed on micas, clays, iron oxyhydroxides, and organic matter (Ames et al. 1983a, Ames et al. 1983b, Ames et al. 1983c, Chabaux et al. 2003), with a sorption capacity ranking as follows: hydrous Fe oxides > well-crystallized goethite >> montmorillonite > kaolinite (Szalay 1964, Manceau et al. 1992). Because sorption is enhanced by greater surface areas, this process has been invoked to account for the increasing radionuclide concentrations with decreasing grain size in soils (Megumi and Mamuro 1977).
- Precipitation of authigenic phases (coefficient Γ_8). The formation of carbonates and Fe-Mn oxyhydroxides can scavenge significant amounts of U from solution where U will be either adsorbed onto surfaces (see above) or incorporated into the crystal structure by isomorphic substitution (see review in Chabaux et al. 2003). When considering bulk soils or stream sediments, the ^{238}U in these secondary phases can represent a significant proportion of the ^{238}U budget (e.g., Plater et al. 1992).
- Dust deposition (coefficient Γ_8). Gain of ^{238}U can also occur via deposition of mineral aerosols. Pett-Ridge et al. (2007) attributed U enrichments up to 531 % in Hawaiian soils older than 150 ka by dust deposition. Pelt et al. (2013) showed that dust deposition can account for up to 25 % of the U and Th budget of basaltic soils in Cameroon. Note that these are extreme scenarios because the parent material (basalt) has a low U content. The contributions from dust to the soil U budget would be less significant in granitic and sedimentary environments. Nevertheless, gain of ^{238}U via dust deposition is accounted for in the model by the parameter Γ_8 .

It is important to note that the numerical models only account for the gain of ^{238}U without differentiating between the different processes of sorption, precipitation or dust deposition that contribute to that gain.

Mobility of ^{234}U :

- Loss during mineral dissolution (coefficient w_4). Congruent dissolution will release ^{234}U at the same rate as ^{238}U (not taking into account the preferential leaching mentioned below). In this case, no fractionation between these isotopes is expected, i.e. $w_4 = w_8$;

- Direct recoil of ^{234}Th and subsequent decay into ^{234}U contributes to enhance ^{234}U mobility compared to ^{238}U . The fraction ^{234}U lost by recoil in Scott et al.'s model is $1 - f_4$;
- Preferential leaching of ^{234}U embedded in recoil tracks. Tracks can provide pathways for migrating solutions to reach ^{234}U thereby enhancing the mobility of ^{234}U compared to undecayed ^{238}U , i.e. $w_4 > w_8$;
- Preferential oxidation of ^{234}U compared to ^{238}U . Computer simulations of the recoiled ^{234}Th motion have shown that in minerals with a low U content, there is a high probability for ^{234}U to be found in the vicinity of oxygen atoms or radicals, making it more prone to oxidation to the hexavalent state resulting in preferential mobilization compared to tetravalent ^{238}U (Adloff and Roessler 1991). This will also contribute to a coefficient w_4 greater than w_8 ;
- Sorption of ^{234}U on mineral phases (coefficient Γ_4). Although untested, it is believed that no fractionation between ^{234}U and ^{238}U occurs during this process. Thus, the adsorbed U will record the $(^{234}\text{U}/^{238}\text{U})$ ratio of the solution (i.e., Γ_4/Γ_8), which in most cases will be greater than 1. This relation is supported by measurements of $(^{234}\text{U}/^{238}\text{U})$ ratios in the exchangeable fraction leached from organic matter, carbonates and crystalline Fe-Mn oxides that were bound to river sediments: all leachates showed values within analytical error of 1.3 (Plater et al. 1992).
- Precipitation of authigenic phases (coefficient Γ_4). As with ^{238}U , ^{234}U can be added to the bulk soil or stream sediment during the precipitation of secondary phases. Because no fractionation between ^{234}U and ^{238}U is believed to occur during secondary mineral precipitation, U in the precipitated phases will record the $(^{234}\text{U}/^{238}\text{U})$ ratio of the solution (in most cases greater than 1), which will define values of Γ_4/Γ_8 .
- Dust deposition (coefficient Γ_4). Similarly to ^{238}U , gain of ^{234}U can occur via the deposition of mineral aerosol. If this is a substantive process for U gain, the Γ_4/Γ_8 ratio represents the $(^{234}\text{U}/^{238}\text{U})$ activity ratio of the dust component.

Considering the processes described above, if sorbed U and authigenic phases can be removed by sequential leaching, we should observe $(^{234}\text{U}/^{238}\text{U})$ activity ratios <1 in weathering products. However, this is not always the case (Lee et al. 2010). A $(^{234}\text{U}/^{238}\text{U}) >1$ could be explained by the Sheng-Kuroda effect (Sheng and Kuroda 1986a, Sheng and Kuroda 1986b). In this case, U-poor residual minerals can be enriched in ^{234}U by implantation from U-rich minerals, which are subsequently removed by dissolution. Note this process excludes zircon as a source for ^{234}U implantation as it is highly resilient to weathering.

Mobility of ^{230}Th :

- Loss during mineral dissolution (coefficient w_0). As ^{230}Th is produced by alpha decay of ^{234}U , it will be located in recoil tracks. Thus, as the mineral dissolves, recoil tracks will be exposed to migrating

solutions allowing release of ^{230}Th . However, Th is highly insoluble and any Th released to the solution is likely to precipitate back and/or be adsorbed on residual minerals. For these reasons, in most studies it is assumed that $w_0 \ll w_4$ or w_8 . Nevertheless, significant ^{230}Th solubilisation can occur in presence of organic acids and colloids and/or at low pH (Langmuir and Herman 1980, Viers et al. 1997, Chabaux et al. 2003, Dosseto et al. 2006a, Dosseto et al. 2006b). For instance, sediments from organic-rich rivers of the Amazon basin are characterised by $(^{230}\text{Th}/^{238}\text{U}) < 1$ (Dosseto et al. 2006a).

- Direct recoil of ^{230}Th during decay of ^{234}U . If decay of ^{234}U occurs within a few tens of nm of the mineral surface, ^{230}Th can be recoiled out of the mineral into the surrounding medium (air or water). The fraction of ^{230}Th lost by recoil is $1 - f_0$. However, as explained above, because of Th low solubility and its high reactivity for mineral surfaces (especially Fe-Mn oxyhydroxides) it is likely that ^{230}Th will be rapidly re-adsorbed onto mineral surfaces.
- Sorption of ^{230}Th from the solution onto minerals or incorporation into secondary minerals (coefficient Γ_0). Th can sorb onto organic matter, clays and Fe-Mn oxyhydroxides (Chabaux et al. 2003), resulting in a gain of ^{230}Th . Based on $(^{230}\text{Th}/^{238}\text{U})$ and $(^{230}\text{Th}/^{234}\text{U})$ activity ratios measured during sequential leaching experiments of river sediments (Plater et al. 1992), it appears that U has a higher affinity for organic matter than Th (thus, Γ_8 or $\Gamma_4 > \Gamma_0$) while the opposite is observed for Fe-Mn oxides ($\Gamma_0 > \Gamma_8$ or Γ_4).
- Dust deposition (coefficient Γ_0). Gain of ^{230}Th can also occur via deposition of mineral aerosols. If this is a substantive process for the gain of U and Th isotopes, then the Γ_0/Γ_8 ratio reflects the $(^{230}\text{Th}/^{238}\text{U})$ activity ratio of the dust component (expected to be greater than 1).

Hence, based on the processes described above, $(^{230}\text{Th}/^{238}\text{U})$ ratios $>$ or < 1 can be observed in weathering products. Because $(^{230}\text{Th}/^{238}\text{U}) > 1$ are more commonly observed, it is likely than conditions where ^{230}Th is insoluble, or where any ^{230}Th lost via recoil is adsorbed onto Fe-Mn oxides, generally prevail.

A corollary from these observations is that at low dissolution rates, and where sorbed nuclides and secondary minerals have been removed, recoil of ^{230}Th should become important and $(^{230}\text{Th}/^{238}\text{U}) < 1$ should be expected in solids. This is similar to what has been proposed to explain $(^{234}\text{U}/^{238}\text{U})$ in waters from New Zealand (Robinson et al. 2004), where loss of ^{234}U is enhanced in situations where physical weathering (comminution) dominates over chemical weathering, thus favouring recoiled ^{234}U over the bulk loss of U.

The concepts and models presented above are used to describe how $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ ratios evolve from initial to observed sets of values over a period of time. The initial $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ are generally taken as those of the parent rock and assumed to represent secular equilibrium (i.e. all U-series activity ratios are equal to 1). Alternatively, when modelling regolith compositions in a weathering profile,

initial ratios can be those of a deeper regolith sample. The amount of time required to evolve from initial to observed isotopic compositions represents the *duration of weathering*. In a weathering profile, this can be equivalent to the age of the weathering front, termed *weathering age*, i.e. the time elapsed since the weathering front was at a given depth (Dosseto et al. 2008b, Dosseto et al. 2012). In river sediments, this is equivalent to the *residence time of sediments in the catchment*, i.e. the time spent by sediments in the catchment since production from the bedrock, integrating storage in weathering profiles and transport in the river (Chabaux et al. 2008, Dosseto et al. 2008a, Vigier and Bourdon 2011).

The set of parameters that best describe the observed ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) ratios is sought for, generally by inverse modelling. The resulting parameters derived from the models are: the duration of weathering and the set of coefficients for each nuclide (depending on the models: f_i , w_i and/or Γ_i , where i is the nuclide considered).

To solve these models, several important assumptions are required:

1. The coefficients for nuclide loss, w , and gain, Γ , are constant over the duration of weathering. This assumption is commonly made in studies that model chemical weathering (e.g. Chamberlain et al. 2005, Ferrier and Kirchner 2008) and laboratory experiments that suggest constant w values for a given mineral (White and Brantley 2003);
2. In the Scott et al. (1992) model, the fraction of recoiled nuclides (coefficient f) is constant over the duration of weathering;
3. Nuclide loss and gain operate on similar timescales;
4. Because of the large number of unknowns, several samples are required and it is assumed their activity ratios differ only as a result of different durations of weathering. Hence, each coefficient for each nuclide is assumed to be constant across samples.

These assumptions are difficult to verify because: (1) conditions for mineral dissolution and precipitation are variable with time, especially over the timescales typically modelled (10^3 - 10^6 years). It is generally assumed that any actual variations will average out over such long timescales, (2) the fraction of recoiled nuclide is dependent on the surface properties of the material, which may vary with time (e.g., as the result of mineral dissolution), (3) the onset of nuclide loss (weathering) could take place significantly earlier than nuclide gain (e.g., illuviation). Nevertheless, even in the early stages of weathering, secondary minerals that contain significant amounts of U are observed (Guthrie and Kleeman 1986, Pelt et al. 2008), (4) constant nuclide gain and loss coefficients between samples are difficult to verify because conditions of mineral dissolution and precipitation can be variable even over small length scales. Despite these strong caveats, previous studies have yielded unprecedented constraints on rates of soil formation and sediment transport (see Chabaux et al. 2008, Dosseto et al. 2008a, Vigier and Bourdon 2011 for recent reviews).

Current investigations, controversies, and gaps in knowledge

This section presents a review of studies using U-series isotopes to constrain timescales of chemical weathering in weathering profiles, rinds, and soil chronosequences. For a review of applications to fluvial sediments, the reader is referred to the reviews by Dosseto et al. (2008a) and DePaolo et al. (2012).

Weathering profiles

When discussing weathering profiles, we must first define a few terms. Here, the *soil* is defined as the top part of the weathering profile, which is mobile as it creeps downhill (colluvial transport). Soil production occurs by physical and chemical weathering of the underlying saprolite or bedrock, often with living organisms playing a preponderant role. The *saprolite* is defined as weathered material that still retains some structural aspects of the bedrock. It is produced at the *weathering front* by physical and chemical weathering of the bedrock. The *regolith* is the ensemble of saprolite and soil, which together constitutes the *weathering profile*. Thus, saprolite production, regolith production and weathering front advance refer to the same process.

The development of weathering profiles is the result of a complex interaction between tectonics, climatic and biotic processes. The thickness and nature of these profiles are an expression of landscape evolution in response to these various mechanisms. The topsoil is of particular importance because it is the basic resource required for sustaining nearly all biological ecosystems including agriculture and human civilisations. Despite this importance, little is known on how fast weathering profiles develop. In contrast, their rate of denudation is well constrained, even at millennial timescales (using cosmogenic isotopes; Brown et al. 1995, Brown et al. 1998). Cosmogenic isotopes can also be used to determine soil production rates (Heimsath et al. 1997, Larsen et al. 2014), however this requires the assumption that the soil thickness is in steady-state, which is seldom verifiable. This approach, by definition, renders it impossible to evaluate soil evolution, i.e. imbalances between production and denudation. Indeed, even if soil thickness has reached a steady-state, how was it achieved? The soil must have been thickening before reaching steady-state. Furthermore, soil production is only one aspect of the development of a weathering profile, with production of saprolite or regolith being the other, even more important aspect. It has been proposed that cosmogenic isotopes could also be used to infer saprolite production rates (Dixon et al. 2009); however, this suggestion also requires the assumption that the entire weathering profile thickness is in steady-state, which is not easily tested.

U-series isotopes offer an alternative to quantify soil and saprolite production rates. Using the model of Dequincey et al. (2002), it is possible to model the amount time that elapsed to produce the observed U-series isotope composition since departure from secular equilibrium. This is equivalent to the time elapsed since the onset of chemical weathering and is termed *weathering age* (Figure 4). By using the weathering age of a given saprolite sample in the profile and its height above the weathering front (i.e. the difference between its depth and the depth of the weathering front), we can infer an average saprolite (or regolith) production rate. This represents the average rate at which the weathering front has propagated between the two depths considered (Figure 4). Similarly, considering a soil sample and using the composition of the underlying saprolite as the initial conditions, we can use the time required to evolve from the U-series isotope composition of the saprolite to that of the soil sample, and the height of the soil sample above the soil-saprolite boundary to infer an average soil production rate (Figure 5).

This approach has been applied to weathering profiles developed over granitic lithologies in tectonically passive, tropical/equatorial regions of south America (Mathieu et al. 1995) and western Africa (Boulad et al. 1977, Dequincey et al. 1999, Dequincey et al. 2002). In Cameroon, Boulad et al. (1977) estimated regolith production rates of 70 mm/ka (Figure 6 and Table 2). In Burkina Faso, while no regolith production rate was estimated, Dequincey et al. (2002) determined weathering ages of ~400-500 ka. In the Amazon, Mathieu et al. (1995) calculated that it took ~300 ka to develop 15 m of regolith in the Amazon. This implies an average regolith production rate of 50 mm/ka (Table 2). These production rates are surprisingly high considering that (i) erosion rates in these areas are most likely <10 mm/ka and (ii) weathering rates are expected to be slow because the weathering front is several tens of meters deep and likely to be isolated from meteoric waters (Gaillardet et al. 1995, Gaillardet et al. 1997, Gaillardet et al. 1999). However, it is important to note that regolith production rates inferred from U-series isotopes are averaged over a timescale that represents the weathering age. Thus while modern weathering rates are most likely slow, they were probably much higher in the past when the weathering front was closer to the surface and subject to higher rainfall and temperatures.

A U-series isotope study was also conducted in Puerto Rico (Chabaux et al. 2013), where the weathering profile is also developed over a granitic parent rock under tropical conditions, but erosion rates are much higher than in western Africa or Brazil (43 ± 15 mm/ka (Brown et al. 1995); 33 ± 8 mm/ka (Riebe et al. 2003)). Calculated regolith production rates were 45 ± 12 mm/ka (Chabaux et al. 2013) (Table 2). This implies that, at the scale of the weathering profile, the loss of regolith is largely balanced by its production from the bedrock. A recent U-series study of stream sediments in the same area shows that a balance between rates of regolith production and erosion is also true at the catchment scale (Dosseto et al. 2014). These results are in agreement with previous work (White et al. 1998, Riebe et al. 2003, Turner et al. 2003a, Pett-Ridge et al. 2009a, Pett-Ridge et al. 2009b, Ferrier et al. 2010). Furthermore, similar regolith production rates over

granitic parent rock in different areas suggest that production is relatively insensitive to erosion rates, and is mostly controlled by the composition of the parent rock and/or climatic conditions.

Dosseto et al. (2012) suggested that the composition of the parent rock is a more important control on regolith production rates than climatic conditions, because they calculated production rates of 334 ± 46 mm/ka for a weathering profile developed over a volcanoclastic sedimentary rock in the same region (and thus very similar climatic conditions) as the granitic profile of Chabaux et al. (2013) (Figure 6 and Table 2). These rates are faster than those for the granitic profile by a factor of ~ 4 .

Studies have also been conducted in temperate regions for weathering profiles developed over granitic lithologies in south-eastern Australia (Dosseto et al. 2008b, Suresh et al. 2013) and shale in north-eastern U.S. (Ma et al. 2010, Ma et al. 2012). In southeastern Australia, the region studied is characterised by a retreating escarpment separating a coastal plain to the east from highland plateaus (elevation ~ 900 m) to the west. Weathering profiles were studied in two different geomorphic contexts: on the escarpment (Dosseto et al. 2008b) and on the plateau (Suresh et al. 2013). Sampling strategies differed between the two studies in that Dosseto et al. (2008b) sampled profiles across the hillslope; while Suresh et al. (2013) sampled profiles on ridgetops so that colluvial transport could be neglected.

On the escarpment, saprolite weathering ages ranged from 0.55 to 6.2 Ma. Values increase downhill with distance from the ridge. These estimates represent the amount of time required to develop ~ 25 m of saprolite and result in saprolite production rates ranging between 4 and 46 mm/ka (Dosseto et al. 2008b) (Table 2). These values are similar to local estimates of denudation rates (9-68 mm/ka; Heimsath et al. 2000), thus demonstrating that the entire weathering profile is in steady-state. This suggests that, over the 0.55 to 6.2 Ma of saprolite development, an equilibrium has been reached between erosion and the conversion of granitic bedrock into saprolite. Similarly, soil weathering ages range from 6 to 38 ka representing the amount of time needed to develop ~ 0.5 -1 m of soil from the underlying saprolite. Soil production rates calculated from U-series range from 12 to 77 mm/ka (Table 2). Here again, it is similar to denudation rates and demonstrates that the soil thickness is in steady-state too. Thus, at this site, the three major interfaces that constitute the weathering profile (atmosphere-soil, soil-saprolite and saprolite-rock) are progressing downward at similar rates. These results are surprising as the escarpment is the most dynamic part of the landscape in this region.

On the plateau, calculated soil weathering ages are up to 30 ka. This represents the amount of time required to develop 30-60 cm of soil from the saprolite. Soil production rates show a much narrower range than at the escarpment, between 10 and 24 mm/ka (Suresh et al. 2013) (Table 2). Here too, production rates are similar to denudation rates inferred from cosmogenic isotopes, effectively demonstrating that soil thickness as also reached a steady-state.

At the Susquehanna/Shale Hills Critical Zone Observatory in north-eastern U.S., Ma et al. (2010, 2013) quantified soil weathering ages and production rates from pits along two opposing hillslopes, developed over a Palaeozoic shale. On the north-facing hillslope, soil weathering ages vary between 7 and 40 ka; representing the amount of time to develop 30-70 cm of soil. This amounts to soil production rates of 17-45 mm/ka (Ma et al. 2010) (Table 2). On the south-facing hillslope, soil weathering ages vary between 12 and 16 ka (to develop 60-80 cm of soil). Inferred soil production rates are 40-50 mm/ka (Ma et al. 2013) (Table 2). These rates are similar to the range observed in granitic environments. This suggests that the composition of the parent rock has little effect on the rate of soil production. However, in the case of Shale Hills, the soil is directly developed over the parent rock, while in granitic environments it is developed over a saprolite. It is thus difficult to use results from the Shale Hills site to assess the role of parent rock composition since pedogenetic processes are quite different from those related to weathering profiles developed over granitic or volcaniclastic sedimentary parent rock.

Soil Chronosequences

Soil chronosequences are defined as a group of soils that differ in age but have similar parent materials and have formed under similar conditions of climate, vegetation and geomorphic position (Jenny 1941). They are particularly useful for U-series isotopic studies if the soil's maximum weathering age is known as they can then be used to calibrate the U-series isotope weathering models.

Pett-Ridge et al. (2007) have studied a chronosequence of soils developed in Hawai'ian tephras with ages ranging from 0.3 to 4100 ka. They showed that the U budget of the soil is largely dominated by dust deposition at older sites, and that Fe-oxides are the main mineral phases carrying U in these soils. Pelt et al. (2013) reached similar conclusions on the role of dust deposition on the U budget of soils in a study of Holocene basaltic flows in Cameroon. These results are a consequence of rapid dissolution of primary phases in basaltic parental material under wet conditions (average annual rainfall: 2500 mm/a). By 20 ka, they are completely exhausted (Crews et al. 1995). In basaltic parent material, U is mostly contained in the groundmass which dissolves very readily, leaving the soil U budget easily dominated by dust deposition and Fe-oxides. Where U is contained in primary minerals that are more resistant to chemical weathering (e.g. biotite, apatite in granitic rocks; illite in sedimentary rocks), the importance of dust deposition and the role of solution-derived secondary phases would be lessened.

The U-series isotope composition of soils developed along a chronosequence has been modelled in a recent study by Keech et al. (2013). The parent material is composed of glacial outwash sediments with deposition ages ranging from 40 ka to 3 Ma. For each soil profile, they averaged the U-series isotope composition of samples collected at different depths and attempted to use the model described in equation (1) to reproduce the average activity ratios, knowing the maximum weathering range of each soil profile (i.e. the deposition age). In doing so, they assumed that the known age of the parent material represents an

average weathering age for the profile. While it is unclear whether an average activity ratio for a given soil profile has any significance in terms of pedogenic processes, the average weathering age of a soil profile should be a value between 0 and the age of the parent material. The authors used the model described by equation (1) but could not reproduce the observed average values for ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$), which showed a decrease with increasing age. To explain this discrepancy, the authors proposed a two-stage model where labile U is mobilised first, followed by the mobilisation of U in crystal lattices during mineral dissolution. This two-stage model assumes that the parent material was in secular equilibrium prior to soil formation. However, in this case, the parent material is an unconsolidated sediment, and is likely to have already undergone significant weathering. This pre-deposition weathering episode would have imparted a disequilibrium to the parent material which would have decayed away only over >300 ka (assuming closed system, which is unlikely during the deposition of an alluvial sediment). Therefore, the greater disequilibrium observed in younger soils may simply be the result of pre-deposition radioactive disequilibria (with ^{234}U and ^{230}Th excesses over ^{238}U) which had not yet decayed away. Thus, there is no need for a two-stage model. Without knowing the U-series isotopic composition of the parent material (which was not sampled), it is not possible to derive reliable time information from this work.

Andersen et al. (2013) have studied the U-series isotopic compositions of soils from a chronosequence formed by glacier retreat in Scotland. The parent material is composed of alluvial sediments deposited in fluvial terraces with ages between 0.1 to 13 ka. At this location, the authors observed that, on average, the ($^{234}\text{U}/^{238}\text{U}$) activity ratio decreased with increasing deposition age, starting with values >1, similarly to what was observed in Keech et al. (2013), but ($^{230}\text{Th}/^{238}\text{U}$) increased with deposition age, from values initially <1. The model described in equation (1) was used to determine ^{238}U dissolution coefficients for 5.6 ka and 13 ka old soils, assuming that the soil weathering age was the same as the deposition age. However, here too the parent material was assumed to be in secular equilibrium. This is unlikely to be the case because soils were developed on fluvial sediments, which were unlikely to be at secular equilibrium at the onset of soil formation (as observed in all fluvial sediments; see the review in Dosseto et al. (2008a)). The decrease in ($^{234}\text{U}/^{238}\text{U}$) with soil age could reflect loss of ^{234}U via recoil, or more likely (as pointed out by the authors) via preferential leaching. The initial ($^{230}\text{Th}/^{238}\text{U}$) <1 in the parent material could be explained as the sediment is likely to be derived from organic-rich hillslopes. The presence of organic acids is known to mobilise Th (Porcelli et al. 1997, Viers et al. 1997, Andersson et al. 1998, Porcelli et al. 2001, Chabaux et al. 2003) and organic-rich soil horizons can exhibit ($^{230}\text{Th}/^{238}\text{U}$) <1 (Dosseto et al. 2008b, Ma et al. 2010, Chabaux et al. 2013, Suresh et al. 2013). The increase in ($^{230}\text{Th}/^{238}\text{U}$) could be explained by the subsequent loss of U during soil development.

While the study of soil chronosequences is an exciting endeavour with a great potential to improve our understanding of soil processes and the use of U-series isotopes, the different aspects of U-series models

need to be carefully considered. For instance, initial conditions (i.e. the composition of the parent material) must be adequately assessed in order to apply the appropriate model parameters.

Weathering rinds

In the early stages of weathering, the parent rock can sometimes develop rinds of weathered material. The measurement of U-series isotopes on a depth profile across the pristine core and the outer weathering rinds can be used to infer how fast the weathering front propagates into the rock. As shown above, it is expected that U is lost preferentially compared to Th and ^{234}U preferentially to ^{238}U , so increasing ($^{230}\text{Th}/^{238}\text{U}$) and decreasing ($^{234}\text{U}/^{238}\text{U}$) activity ratios, respectively, should develop with time. However, in a study of weathering rinds developed on a basaltic clast from a 125 ka-old alluvial terrace in Costa Rica, Pelt et al. (2008) observed the opposite with ($^{230}\text{Th}/^{238}\text{U}$) <1 and ($^{234}\text{U}/^{238}\text{U}$) >1 in the most extensively weathered parts of the rinds. This was interpreted as the result of (i) the conservative behaviour of Th and (ii) external input of U from soil solutions having ($^{234}\text{U}/^{238}\text{U}$) >1, with minimal loss of U during weathering. The input of U was modelled resulting in a rind formation rate of 0.5 ± 0.2 mm/ka (Table 2). In another study, Ma et al. (2012) also found ($^{230}\text{Th}/^{238}\text{U}$) <1 and ($^{234}\text{U}/^{238}\text{U}$) >1 in weathering rinds from a basaltic clast from Guadeloupe Island. They inferred a rind formation rate of 0.18-0.24 mm/ka (Table 2). These rates are three orders of magnitude lower than what has been inferred considering the scale of the weathering-profile development for basaltic lithologies (Dosseto et al. 2012). As explained in Navarre-Sitchler and Brantley (2007), this apparent discrepancy stems from the fractal nature of the weathering advance rate, its value being largely controlled by the length scale over which it is measured. This is a consequence of the variable spatial resolutions used to measure the surface area of the weathering front (from the 10^{-3} m scale when studying weathering rinds to the meter scale when investigating weathering profiles). Navarre-Sitchler and Brantley (2007) showed that it is possible to compare weathering advance rates across length scales by calculating the roughness of the weathering front at each length scale, using the fractal dimension characteristic of the weathering advance rate (for instance, ~ 2.3 for basaltic weathering).

In a weathering profile developed over a granitic corestone in Puerto Rico, Chabaux et al. (2013) also quantified the rate at which weathering-rind formation advances into the corestone and estimated a value of 52 ± 13 mm/ka. Interestingly, this is similar to the saprolite production rate inferred in the same profile (Table 2). This can be explained by the small length scales of weathering-rind development studied by Pelt et al. (2008) and Ma et al. (2012) measured in millimeters, compared to the weathering rinds studied by Chabaux et al. (2013), which cover a length scale similar to that of the weathering profile developed above them.

Implications for landscape evolution

A compilation of calculated regolith and soil production rates, similar to the one shown in Dosseto et al. (2012), allows us to make several observations concerning the development of weathering profiles (Figure 6). Note that these observations need to be considered with caution, given the small number of studies published so far. However, they hint at some aspects of landscape evolution that are worth investigating.

It has been known for a long time that different rocks weather at different rates, depending on the susceptibility to dissolution of the minerals that compose them. This is illustrated on Figure 6, where in Puerto Rico, regolith production over a volcanoclastic sedimentary rock occurs at a rate more than six times faster than over granodiorite. However, parent material composition does not appear to play a strong role for soil production: soils over a shale are produced at about the same rate as those produced over a granitic rock (Figure 6). This may imply that soil production is mostly driven by physical weathering, via the mechanical action of plants and animals, rather than by chemical weathering.

The role of climate (runoff, temperature) on regolith production is not clear from results shown in Figure 6: granitic profiles seem to develop at similar rates across a range of climatic conditions. While it is possible that regolith production rates that are lower than expected in Africa and the Amazon may be the consequence of thick weathering profiles shielding the weathering front from meteoric waters, profiles in Puerto Rico and south-eastern Australia have similar thicknesses and production rates despite very different climatic conditions.

Erosion rates in lowlands of western Africa and the Amazon are expected to be <10 mm/ka (Gaillardet et al. 1997, Wittmann et al. 2010). In contrast, Larsen (2012) has estimated long-term hillslope erosion rates in the Rio Icacos basin of Puerto Rico to be ~ 75 mm/ka, mostly driven by landslides. Despite about an order of magnitude difference in erosion rates, regolith production rates for these granitic profiles are relatively similar. They exceed erosion rates in tropical lowlands, while they are similar to or lower than erosion rates in Puerto Rico. This could suggest a decoupling between the surface (where erosion occurs) and the weathering front. The advance rate of the weathering front seems to be most sensitive to the composition of the parent material, showing similar values for granitic profiles across a range of climatic conditions and erosion rates.

Gaps in knowledge

The models described above are intended to track the U-series isotope composition of minerals derived from the parent rock, whether they are residual primary minerals or secondary minerals formed during incongruent dissolution of primary minerals. Existing studies have focused on bulk material (regolith, soil, sediments). As explained above, the regolith is a complex mixture of primary minerals (derived from the

parent rock), secondary minerals precipitated from soil pore water (e.g. carbonates and Fe,Mn-oxyhydroxides), allochthonous minerals (via dust deposition), and organic matter (Figure 3). Each of these phases is likely to have its own U-series isotope composition. Thus, the application of the U-series models is complicated by the contribution of each of these components to the isotopic composition of the bulk sample. Future works should investigate techniques to remove these phases either physically (e.g. mineral separation; (Menozzi and Dosseto 2013, Rihs et al. 2013)) or chemically (e.g. sequential extraction; (Schultz et al. 1998, Blanco et al. 2004, Martin et al. submitted)). Until then, we will still be relying on which ever phases control the U budget of the samples. If the U budget is controlled by only a single primary phase or a secondary phase derived from primary minerals, the models may provide reliable results. If the U-budget is controlled by more than one primary phase or secondary phase derived from primary minerals, there might be some noise in the data that make the models less straightforward to apply. If controlled by a mixture of primary and associated secondary minerals, as well as solution-derived secondary minerals, allochthonous minerals, or organic matter are involved, it is likely that the models will yield less than straightforward information. Finally, if the U budget of the samples is controlled by solute-derived secondary minerals, allochthonous minerals, or organic matter, the models will provide meaningless information in term of weathering age, as defined above. Thus, the future of this technique depends on our ability to understand the U-series contributions from the various components involved and how they impact the overall compositions from which the models are developed.

Conclusions

U-series isotopes in weathering products (weathering rinds, regolith, sediments) allow us to place time constraints on weathering processes. These then can be used to determine the rate of formation of weathering profiles (*regolith production rates*). Results from available studies, when combined with other tools like cosmogenic isotopes, provide unprecedented insights on the development of weathering profiles and landscape evolution. Results from these studies show that climate seems to have a secondary role on regolith production rates. Instead, the primary control on regolith production appears to be the composition of the parent material. Under tropical climates, for instance, regolith can be produced ~6 times faster over a volcanoclastic sedimentary rock than over a granodiorite parent. Conversely, soil production seems to be relatively insensitive to the parent material composition: under temperate climates, soil is produced at the same rates over shale and granodiorite. Finally, regolith production rates are similar for sites that show a range of erosion rates. This suggests a decoupling between the land surface and the weathering front. In this case, the topography of the weathering front would be determined by the lithology, while the surface topography is determined by denudation in response to climatic and tectonic conditions.

Several studies have emphasized the role of dust deposition on weathering profile development, and in particular on the uranium budget of the soil. While this is taken into account in existing models U-series isotopic evolution, further work is needed to improve the robustness of the information derived from these models. In order to achieve this objective, innovative chemical and/or physical protocols for sample preparation are important avenues to explore.

Finally, soil chronosequences represent fascinating natural laboratories to test the application of U-series isotope methods and to further improve the quality of information that U-series models provide. However, these studies need to be carefully undertaken, with a full understanding of the assumptions required by each different model.

With these considerations in mind, it is clear that, combined with other geochronological and geochemical techniques, U-series isotopes supply us with an ability to better understand the evolution of the Earth's surface. As summarised in this contribution, more than ten years of studies on the topic illustrate the unique prospects that this technique offers.

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Cross-references

Aquifer Characteristics (U-Series)

Cements, Pedogenic (U-Series)

Cosmogenic Nuclide Dating

Mass Spectrometry

Paleosol

Radiation and Radioactivity

Radiation Defect

U-Series Dating

Figure 1: Uranium-238 decay chain. Each nuclide half-life is shown under its name and expressed in years (yr), days (d), hours (hr) or minutes (min). Two types of radioactive decay occur in the chain: α (decay energy shown under the symbol) and β .

Figure 2: Schematic representation of various scenarios of alpha-decay. In (a), case (a1) occurs when ^{234}Th (black dot) is directly recoiled out of the source mineral (red circle). In case (a2), the direction of recoil from ^{238}U (grey dot) is such that ^{234}Th is embedded further into the source mineral. In case (a3), ^{234}Th is embedded in an adjacent mineral (blue circle). In all cases, ^{234}Th then decays rapidly into ^{234}U . In (b), a fluid fills in the pore space. In case (b1), the ^{234}Th is directly-recoiled into the fluid which readily transports the subsequently formed ^{234}U . In case (b2), mineral dissolution (light red area) exposes a recoil track such that the embedded ^{234}U can be leached out of the track. In case (b3), the recoil track in the adjacent mineral is exposed to the fluid and the embedded ^{234}U leached away.

Figure 3: Schematic representation of the role of the different components of weathering products to their U-series isotope composition. U-poor minerals (e.g. quartz) do not contribute to the radioactive disequilibrium of soils or sediments because of their low U concentration. U-rich minerals that weather readily (e.g. monazite) do not contribute to the radioactive disequilibrium of soils or sediments because as they are entirely dissolved and their entire ^{238}U , ^{234}U and ^{230}Th isotope budget is transferred to the soil-forming solution. Insoluble U-rich minerals (e.g. zircon) do not contribute to radioactive disequilibrium because they are highly resistant to weathering. However, these minerals can contribute to radioactive disequilibrium if (i) they are highly metamict, which favours release of ^{238}U and its decay products, and (ii) they implant ^{234}U and ^{230}Th to adjacent minerals as a result of decay. U-rich primary minerals that weather, but survive weathering (e.g. muscovite or apatite), as well as secondary minerals derived from the incongruent dissolution of these primary minerals provide the dominant control on the U-series isotope composition of soils or sediments. In addition, authigenic phases (as secondary minerals precipitated from soil pore water) and organic matter inherit the U-series isotope composition of the solution from which they formed and can also contribute to the U-series isotope composition of the soil or sediments.

Figure 4: Conceptual definitions of the *weathering age* and the *saprolite/regolith production rate*. If one considers the downward propagation of the weathering front into bedrock (lower dashed line), the weathering age, τ_{sap} , of a given saprolite sample (red dot) is the amount of time required for the weathering front to migrate over the distance h_{sap} , which is the height of the sample above the current weathering front. The saprolite or regolith production rate ϵ_{sap} (in mm/ka) averaged over the distance h_{sap} , can then be calculated by dividing h_{sap} (in mm) by τ_{sap} (in ka). Modified from (Dosseto et al. 2008b).

Case 1

Case 2

Figure 5: Conceptual definitions of the *soil weathering age and production rate*. If one considers a given soil sample (yellow dot), the soil weathering age, τ_{soil} , is the amount of time required for the soil-saprolite boundary (dashed line) to migrate downward over the distance h . The distance h represents the height of the soil sample above the current soil-saprolite boundary. Two cases are considered: in Case 1, bioturbation is neglected and the soil production rate ε_1 , averaged over the distance h , is the ratio of h over τ_{soil} . In Case 2, bioturbation is considered and the soil production rate ε_2 , averaged over the entire soil thickness H , is the ratio of H over τ_{soil} . In the latter case, the soil thickness must be in steady-state in order to obtain a meaningful production rate. Modified from (Dosseto et al. 2008b)

Figure 6: Compilation of U-series-isotope-derived of regolith (closed rectangles) and soil (open rectangles) production rates (in mm/ka).

Table 1. Parameters used for U-series isotope models

Parameter	Description	Units
N_g, N_d, N_0	Concentrations of ^{238}U , ^{234}U and ^{230}Th , respectively	atoms.g ⁻¹
$\lambda_g, \lambda_d, \lambda_0$	Decay constants for ^{238}U , ^{234}U and ^{230}Th , respectively	a ⁻¹
w_g, w_d, w_0	Dissolution coefficients for ^{238}U , ^{234}U and ^{230}Th , respectively	a ⁻¹
$\Gamma_g, \Gamma_d, \Gamma_0$	Gain coefficients for ^{238}U , ^{234}U and ^{230}Th , respectively	a ⁻¹
f_d, f_0	Fraction of recoiled ^{234}Th (and thus ^{234}U) and ^{230}Th , respectively	unitless

Table 2. Compilation of regolith and soil production rates from U-series isotope studies

Location	Parent rock	Regolith (or saprolite) production rate (mm/ka)	Soil production rate (mm/ka)	Reference
<i>Weathering profiles</i>				
Cameroon	Granite	70	n/d	Boulad et al. 1977
Burkina-Faso	Granodiorite	30-40	n/d	Dequincey et al. 2002
Amazon (Brazil)	Granite	50	n/d	Mathieu et al. 1995
Icacos (Puerto Rico)	Granodiorite	45 ± 12	n/d	Chabaux et al. 2013
Bisley (Puerto Rico)	Volcaniclastic sedimentary rock	334 ± 46	n/d	Dosseto et al. 2012
Nunnock (Australia)	Granodiorite	4-46	12-77	Dosseto et al. 2008
Frogs Hollow (Australia)	Granite	n/d	10-24	Suresh et al. 2013
Shale Hills (PA, USA)	Shale	n/d	17-50	Ma et al. 2010, 2013
<i>Weathering rinds</i>				
		Rind formation rate (mm/ka)		
Costa Rica	Basalt	0.5 ± 0.2		Pelt et al. 2008
Guadeloupe	Basalt	0.18-0.24		Ma et al. 2012
Icacos (Puerto Rico)	Granodiorite	52 ± 13		Chabaux et al. 2013