Assessment of sequential extraction and mineral separation for studying uranium-series isotopes in Regolith

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Assessment of Sequential Extraction and Mineral Separation for studying Uranium-Series Isotopes in Regolith

A thesis submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy

By

Davide Menozzi MSc.

From

University of Wollongong

School of Earth and Environmental Sciences,

Faculty of Science, Medicine and Health

February 2016
I, Davide Menozzi, affirm that this thesis is the result of my own work unless otherwise referenced or acknowledged. This work has not been submitted for a degree to any other institution or university.

Davide Menozzi

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Abstract

In a weathering profile, the variation with depth of the uranium-series (U-series) isotopic composition can be modelled to estimate regolith production rates. Secondary phases precipitated from solution (solution-derived phases) and organic matter present in regolith may introduce uncertainties in the model and decrease the accuracy of regolith production rates. A pre-treatment to remove these phases could address this drawback. It is also necessary that the pre-treatment does not affect the isotopic composition of minerals derived from the bedrock (bedrock-derived phases). This thesis aims at developing the method to estimates regolith production rates using U-series isotopes. This was done by testing sequential extraction (a chemical procedure used to remove specific solution-derived phases and organic matter from regolith) and mineral separation as methods to isolate bedrock-derived phases. In addition, U-series, major elements and mineralogical analyses were used together to explore U-series isotopes fractionation during pedogenesis.

In Chapter 2, sequential extraction was applied to a basaltic weathering profile. During pedogenesis, the bulk soil experienced addition of solution-derived phases and organic matter containing U-series isotopes; sequential extraction removed these phases and nuclides retained in them. In contrast, the saprolite did not gained nuclides during its formation and sequential extraction resulted in bedrock-derived mineral dissolution. In this type of regolith, sequential extraction is recommended only for horizons where solution derived-phases and organic matter have been gained (in this case study, the soil).

In Chapter 3, sequential extraction and separation of quartz and biotite were applied to a granitic weathering profile. Sequential extraction did not result in removal of major phases. However, it seemed to remove a pool of bedrock-derived U and Th, possibly retained in grain boundaries and/or inclusions. In this case, we do not recommend sequential extraction on the granitic regolith. Quartz separates displayed a general loss of U throughout the profile, whereas Th was possibly adsorbed in the saprolite. This mineral showed great potential to study U-series nuclides fractionation during pedogenesis; however, a treatment to remove nuclides adsorbed on quartz surface is needed. In contrast, biotite acted as a “sponge” for U-series isotopes and is not suitable for U-series isotope analyses. This study suggests that mineral separation can contribute to better understand U-series nuclide fractionation during pedogenesis.
In Chapter 4, a podzol developed on sandstone and characterized by an eluviated E horizon and an illuviated B horizon was studied. Here, sequential extraction did not affect the E horizon; this is because secondary phases and organic matter were not considerably present due to eluviation. In the B horizon, it removed, at least partially, illuviated U-series isotopes associated with solution-derived phases and organic matter. Analysing the residue of sequential extraction instead of bulk material could improve the accuracy of regolith production rates inferred using U-series isotopes. In quartz separates, continuous loss of U and Th with decreasing regolith depth was observed, whereas no evidence suggested gain of U and/or Th. This suggests that quartz recorded the fractionation of U-series isotopes during regolith formation and could be a candidate mineral to estimate regolith production rates (e.g. quartz residence time in regolith).

Although regolith production rates inferred using U-series isotopes are commonly estimated on bulk regolith, isolation of bedrock-derived phases offers a solution to improve the accuracy of this technique. Sequential extraction and mineral separation revealed to be potential tools to achieve this.

This thesis also displayed that processes not reflecting commonly expected U-series isotope mobility (i.e. $^{234}\text{U} > ^{238}\text{U} >> ^{230}\text{Th}$) played a major role in the evolution of the isotopic composition of the three regolith examined in this study. This suggests that the mobility of U-series isotopes in regolith may need to be reconsidered and more emphasis might need to be placed on underrated fractionation processes, such as greater mobilization of $^{230}\text{Th}$ relative to $^{238}\text{U}$ caused by alpha recoil.
1 Introduction

1.1 Background

Landscapes are dynamic systems created and continuously re-shaped by the interaction among the lithosphere, atmosphere, biosphere and hydrosphere. Tectonic processes, physical and chemical weathering and erosion are the main mechanisms controlling the evolution of landscape. Tectonics creates mountain ranges and expose to the Earth’s surface new substrata, such as rocks. Physical and chemical weathering disintegrates rocks and, in combination with biological activity, result in the formation of soil and sediment. Erosion and sediment transportation work together and produce landforms such as valleys and river systems. Organisms (i.e. biosphere) interact with all these processes; for instance, vegetation plays a role in weathering, can stabilize soil on hill slopes and mix the upper part of weathering profiles (Gray, 1974). These processes continuously take place over geologic as well as human timescales and result in the landscape we observe today.

This thesis focuses on chemical weathering, particularly on the formation of regolith profiles, namely the ensemble of soil and saprolite. The aim is to develop further and increase the robustness of geochronological method to estimate regolith production rates using the uranium-series (U-series) isotopes. More accurate rates of regolith production can provide information to better understand soil sustainability, defined as the balance between erosion and production (Amundson et al., 2015). Moreover, weathering processes are known to consume carbon dioxide and they play a role on the global carbon-cycle (Walker et al., 1981).

Weathering breaks down parent materials and over geologic timescale they are converted into regolith, in a process called pedogenesis. During this process, the elemental and isotopic composition progressively varies with depth. The compositional variations through a regolith can be used as an archive that represents different stages of the weathering, represented by diverse horizons: incipient weathering (weathered bedrock), intermediate weathering (saprolite) and intense weathering (soil). Radioactive isotope systems can be used as geochemical tools to constrain time information from these
archives (Cornu et al., 2009; Vasconcelos, 1999). For instance, the radioactive U-series isotopes enclose a “built-in chronometer”, represented by their half-lives (Rosholt et al., 1966). The isotopic composition of these nuclides through a weathering profile can be used to estimate regolith production rates (Dosseto et al., 2008b).

In the last twenty years, the U-series isotopes have been used to estimate regolith production rates (e.g. Chabaux et al., 2011; Dosseto et al., 2012; Ma et al., 2012; Mathieu et al., 1995). However, this method has been applied only in few cases; more studies are needed to better understand the functioning of this geochemical tool and to develop it. For instance, pedogenesis removes but also redistributes and/or introduces elements in a profile, generating a regolith that is a complex mixture of minerals, secondary phases, organic matter, and aqueous solution. Because regolith production rates estimated using U-series isotopes are based on models that follow the isotopic evolution with depth of minerals derived from the underlying bedrock, some of these processes, such as redistribution, introduction of secondary phases and organic matter, increase uncertainties. This issue can be limited by using pre-treatments that selectively remove unwanted phases (Dosseto et al., 2008b; Suresh et al., 2014).

This thesis investigates two possible approaches for the removal of i) secondary phases not derived from the bedrock or redistributed in the regolith by pedogenic processes and ii) organic matter. Two different approaches are applied to three weathering profiles developed over basalt, granite and sandstone: sequential extraction and mineral separation (handpicking). The aim is to improve the accuracy of regolith production rates estimated using the U-series isotopes. Moreover, the study contributes to better understand the mobility of the U-series isotopes in regolith profiles.

This chapter aims at providing a summary of the information needed to understand the importance and functioning of the U-series isotopes as a tool to investigate regolith production processes, and to comprehend the following chapters, which are in paper format. First, section 1.2 discusses the importance of chemical weathering processes for the landscape and human society. Second, section 1.3 reviews processes controlling the development of weathering profiles and geochemical tools used to estimate regolith production rates. Finally, in section 1.4, the characteristic of the U-series isotopes, their
geochemical behaviour in the environment and the model used to estimate regolith production rates are presented.

1.2 The carbon-cycle and chemical weathering

Over 100 years ago, Arrhenius (1896) recognised that the concentration of CO$_2$ in the atmosphere plays an important role in controlling the temperature of the Earth’s surface. In turn, Earth’s surface temperature affects the climate. Because human activities have been releasing great amounts of CO$_2$ in the atmosphere, today’s scientific research aims at understanding the processes controlling the C-cycle and ultimately the impact of human activities on it (Berner, 1994; Falkowski et al., 2000; Friedli et al., 1986; Marcott et al., 2014). For instance, it is important to comprehend how much CO$_2$ emitted by human activity remains in the atmosphere and how much is transferred in other C reservoirs.

The atmospheric CO$_2$ is one of the main reservoirs of the C-cycle along with lithosphere, hydrosphere and biosphere. Carbon is transferred from one reservoir to another via biogeochemical processes over various time scales. An important geochemical process is chemical weathering, which consumes atmospheric CO$_2$. This thesis focuses on chemical weathering processes and in particular on rates of regolith production. This section summarises the processes controlling the C-cycle, paying particular attention to chemical weathering processes.

1.2.1 Carbon cycle

The carbon cycle is the redistribution of C among its reservoirs. Figure 1.1 schematically represents the major reservoirs (represented by boxes) and the main processes (arrows) that transfer C from one reservoir to another. Carbon transfer processes operate over two different timescales. On the long term, in the order of millions of years, atmospheric CO$_2$ is consumed by continental chemical weathering of silicate minerals. Silicate minerals containing Ca and Mg react with atmospheric CO$_2$; these compounds dissolve during weathering, are transported through river systems into the oceans and are ultimately buried on the seafloor as Ca and Mg carbonates (Berner and Kothavala, 2001). Over a similar time scale, an inverse process takes place: C is transferred from the lithosphere to the atmosphere by metamorphic processes. Additionally, removal of atmospheric C by
biological activity and following storage in fossil deposits (oil, coal and natural gas) occurs on similar time scales.

Over a time scale ranging from years to centuries, C is exchanged between atmosphere, the oceans and biosphere through biogeochemical processes. The atmosphere and the ocean exchange C mostly by diffusion at the water-air interface producing dissolved inorganic carbon (DIC). The ocean contains approximately 50 times more C than the atmosphere. Carbon dioxide is more soluble in cold and salty waters; interacting with the thermohaline ocean circulation, a large amount of DIC is contained in deep oceans for tens to hundreds of years and is prevented to equilibrate with the atmosphere (Broecker, 1997). This mechanism is also referred to as solubility pump.

Phytoplankton photosynthesis is another important process that promotes atmospheric C transfer into oceans. This is because it consumes and decreases the concentration of DIC at the ocean surface and, therefore, promotes CO₂ absorption from the atmosphere. Nearly 25% of biologically-fixed C is transferred in deep ocean, converted to DIC by biologic processes (e.g. organic decay) and subsequently confined in deep waters (Falkowski et al., 2000; Falkowski et al., 1998). In addition, some phytoplankton species produce carbonate shells that decrease the DIC concentration in surface water and, once the organisms perish, sink and sediment on the ocean floor (Falkowski et al., 2000). These two processes are referred to as biological pump and together with the solubility pump result in the deep ocean (>300 m) concentrating DIC and retaining approximately 97% of total ocean C (Houghton, 2007). However, the capacity of deep ocean to keep DIC in solution is finite; therefore, on time scales of hundreds of years CO₂ is returned from the ocean to the atmosphere by diffusion processes and through the thermohaline ocean circulation (Falkowski et al., 2000).

The pedosphere exchanges C with the atmosphere over relatively short time scales. Carbon dioxide is used by photosynthetic organisms, stored in organic matter and returned to the atmosphere via respiration, decomposition and other processes such as fire (here incorporated in the term respiration for simplicity; Falkowski et al., 2000). The atmosphere and terrestrial vegetation contain similar amount of C, while soils are estimated to store two/three times this amount (Houghton, 2007). Additionally, in the last
200 years C cycle was affected by human activity through burning of fossil C deposits. This resulted in an increase in the concentration of C in the atmosphere.

This thesis focuses on chemical weathering processes. In particular, understanding the rate at which chemical weathering occurs can provide information on long-term budgets of C cycling and CO₂ consumption.

Figure 1.1. Schematic representation of the C cycle. Dashed lines represent processes that transfer C from a reservoir to another over time scales comprised between years and centuries. Solid lines indicate processes occurring over thousands and millions of years.

1.2.2 Chemical weathering

A general definition for chemical weathering is the decomposition and disintegration of rocks by chemical reactions that result in the formation of different material, such as regolith (Al-Agha, 2006). These reactions are carried out mainly by aqueous solution and the substances contained in it (e.g. solutes and suspended material). Rock-forming minerals are mostly silicates; chemical weathering changes their elemental composition and modifies the mineralogy of the resulting material. For instance, olivine is a labile mineral and weathering easily attacks its crystalline structure, dissolves and/or re-arranges elements such as Mg and Fe, and converts it into clays and/or Fe-oxides.
(chlorites, smectites, montmorillonites, oxides and/or hydroxides; Delvigne et al., 1979). Over geological time scales, these processes convert rocks into weathering products and produce regolith. In addition, chemical weathering processes shape the Earth’s surface and provide elements and nutrients to ecosystems.

Chemical weathering occurs through five main types of reaction: i) hydrolysis, ii) carbonation, iii) redox, iv) solution and v) ion exchange (Fitzsimons, 2001). Hydrolysis is the reaction of protons, $H^+$, and hydroxide ions, $OH^-$, in solution with mineral components. A simple example is the dissolution of fosterite in water:

$$Mg_2SiO_4(sol) + 4H^+(aq) = 2Mg^{2+}(aq) + H_4SiO_4(aq)$$

This reaction does not produce solid residues and is referred to as congruent dissolution.

Carbonation is another type of chemical weathering reaction, involving the reaction of a mineral and dissolved $CO_2$. This results in the removal of a metal from the mineral and the formation of bicarbonate in solution (Fitzsimons, 2001). In a regolith, $CO_2$ dissolved in pore water is derived by the atmosphere and by biological activity. Biological activity can dramatically increase the $CO_2$ concentration in regolith air and, therefore, in regolith pore water. The latter process makes carbonation reactions important in regolith weathering. An example of carbonation reaction is the dissolution of feldspar:

$$6KAlSi_3O_8 + 28H_2O + 4CO_2(aq) \rightarrow 4K^+ + K_2Al_4(Si_6Al_2O_{20})(OH)_4 + 4HCO_3^- + 12H_4SiO_4$$

**feldspar** **water** **carbon dioxide** **illite** **bicarbonate** **silica**

In this reaction, feldspar reacts with dissolved $CO_2$ species (DIC) and produces a clay mineral, illite, $K^+$, $HCO_3^-$ ions, and $SiO_2$. The reactions in which a mineral is converted into secondary phase, such as a clay, are referred to as incongruent dissolution.

The last reaction type is redox and in weathering processes commonly involves the oxidation of Fe- and Mn-bearing minerals. Oxidation is defined as the transfer of one or more electrons from a reductant molecule or atom to an oxidizer species, which often is gaseous or dissolved molecular-oxygen. The weathering products are commonly oxides or, in presence of water, hydroxides. The reddish colour of some rocks and soils are the classical example of the presence of Fe-oxide and -hydroxides produced by oxidation of
Fe-bearing minerals. Redox processes are also mediated by biological activity. Bacteria produce metabolic energy from chemical oxidation and reduction of elements such as Fe and Mn contained in minerals (Gadd, 2010; Nordstrom and Southam, 1997; Thamdrup, 2000). This is an example of how biological activity contributes to weathering processes.

Hydrolysis, carbonation and redox reaction play together during weathering to convert bedrocks into regolith. Despite this thesis will not directly focus on these processes, their understanding is fundamental to comprehend this study. In fact, chemical weathering processes are the reactions that mobilize the U-series isotopes in the environment.

### 1.2.3 The consumption of CO₂ by chemical weathering

Nearly 90% of the Earth’s crust is made of silicate minerals such as quartz, feldspar, mica, olivine and clay (Jung et al., 2010). Therefore, the alteration of these minerals represents most of the weathering processes operating on the Earth’s surface. The chemical reaction that occurs during weathering is exemplified by the following series of reactions:

- **Reaction 1)** \[ \text{CO}_2(\text{gas, atm}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3(\text{sol}) = \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \]
- **Reaction 2)** \[ \text{Mg}_2\text{SiO}_4(\text{sol}) + 4\text{H}^+(\text{aq}) = 2\text{Mg}^{2+}(\text{aq}) + \text{H}_4\text{SiO}_4(\text{aq}) \]
- **Reaction 3)** \[ \text{Mg}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq}) = \text{MgCO}_3(\text{sol}) + \text{H}^+(\text{aq}) \]

Atmospheric CO₂(\text{gas, atm}) is dissolved in water and forms H₂CO₃(sol) (carbonic acid), which is dissociated in a proton H⁺(aq) and HCO₃⁻(aq), producing acidic solution (reaction 1). When a silicate mineral, here exemplified by the fosterite (Mg₂SiO₄(sol)), interacts with acidic solution, it is hydrolysed resulting in its dissolution (reaction 2). Reaction 3 rarely occurs *in situ*; free Mg²⁺(aq) and HCO₃⁻(aq) are transported in solution by river systems into the oceans and eventually precipitated as a solid phase (magnesium carbonate). Similar reactions are possible with different cations, in particular Ca²⁺. From a global C cycle perspective, this series of reaction sequestrate atmospheric CO₂ by producing carbonate minerals that are buried in marine sediments (Berner and Maasch, 1996; Kump et al., 2000; Velbel, 1993). This shows the importance of chemical weathering in regulating the atmospheric CO₂ concentration.
1.2.4 Carbon fluxes among major C reservoirs

Compiling the amount of C contained in the reservoirs and estimating fluxes among them is very complex; the main reason is that fluxes operate at very different time scales. For instance, the transfer of C from vegetation to atmosphere via respiration takes seconds, while carbonate burial through chemical weathering of silicate may take thousands or millions of years. This is the reason why major scientific studies consider C fluxes on different time frames, typically in the order of years to centuries, or thousand to millions of years (e.g. Houghton, 2007; Kump et al., 2000).

Figure 1.2 shows the carbon cycle, the estimated mass of C in the different reservoirs and the rate of C exchange among them. The values are compiled from two articles that considered carbon fluxes on different time scales. Houghton (2007) assessed short-term carbon cycle and focused on the interactions among atmosphere, oceans, terrestrial ecosystems and fossil carbon. In contrast, Kump et al. (2000) estimated global C fluxes on the long term, concentrating on the one hand on chemical weathering processes, and on the other hand on metamorphism, volcanism and diagenesis.

The greatest C reservoir is the lithosphere, containing 80 million Pg (that is peta grams = $10^{15}$ g), followed by the oceans, fossil carbon, terrestrial ecosystems and soil. The atmosphere is the reservoir containing the least mass of C; this suggests that it is also the most sensitive to variation in carbon fluxes, hence, other reservoirs can significantly influence atmospheric C content (Mörner and Etiope, 2002).

Over the short term, the exchange of carbon between the terrestrial ecosystem and the atmosphere is balanced, as modern C fluxes resulting from respiration and photosynthesis are nearly equal (Figure 1.2). Similarly, the C fluxes occurring between the ocean and the atmosphere are nearly equal. The transfer of C from the fossil reservoir to the atmosphere by human activity is not negligible and it equals ~5% of the C transferred by respiration. For simplicity, the term respiration incorporates other C fluxes produced by decomposition and natural fires, which are linked to biological activity (Houghton, 2007).

The C flux estimates show that if human C input to the atmosphere via combustion of fossil fuels was excluded, the carbon cycle would be relatively equilibrated, at least on
short time scales. However, human activity mobilizes carbon from the fossil reservoir to the atmosphere and results in an increase of the mass of atmospheric C.

Over longer time scales, C fluxes due to chemical weathering on the one hand, and metamorphism and volcanism on the other hand, are one to three orders of magnitude smaller than the processes occurring on shorter time scales. However, long term C fluxes are thought to significantly affect the C content of the atmosphere and oceans only over thousands of years (Kump et al., 2000; Mörner and Etiope, 2002). In general, long timescale C fluxes act as negative feedbacks toward short timescale fluxes; these dynamics maintain the Earth system relatively stable on the long-term, while fluctuations occur over short-term (Kump et al., 2000).

The role played by chemical weathering in the C cycle is not well understood (Kump et al., 2000). This thesis aims at improving our understanding of the U-series isotopes mobility during weathering processes, particularly during pedogenesis. This information can be potentially used to estimate weathering rates and, therefore, to better understand the relationship between climate (e.g. atmospheric CO₂ fluxes) and chemical weathering.
Chemical weathering has been hypothesised as a major process at play during climate cooling and the formation of continental ice-sheets that has occurred in the late Cenozoic. Raymo and Ruddiman (1992) hypothesised that this cooling episode is related to the tectonic uplift of the Tibetan plateau, which, among other effects, increased the amount of rock surface available for chemical weathering and erosion. In turn, rates of global chemical weathering may have increased; this may have resulted in greater consumption of atmospheric CO₂ compared to the period antecedent the cooling event and produced a decrease in the atmospheric CO₂ concentration. The lower atmospheric CO₂ concentration
may have caused lower global temperatures and, subsequently, the formation of continental ice sheet.

The hypothesis formulated by Raymo and Ruddiman (1992) is supported by two successive works that investigated the influence of denudation rates on chemical weathering rates at a global scale (Hilley et al., 2010; West, 2012). Hilley et al. (2010) modelled how denudation and mineral-dissolution kinetic reaction influence chemical weathering of silicate minerals; they considered different landscape settings and diverse silicate minerals in order to obtain an outlook at a global scale. Hilley et al. (2010) confirmed that in response to increasing denudation rates, due for instance to the uplift of the Tibetan plateau, rates of chemical weathering of silicate minerals are expected to increase, resulting in greater consumption of atmospheric CO$_2$. In a later article, West (2012) inferred that chemical weathering can significantly affect the atmospheric CO$_2$ concentration only during periods of high denudation rates, such as during the uplift of the Tibetan plateau.

The works by Raymo and Ruddiman, Hilley et al. and West show the importance of better understanding the mechanisms controlling chemical weathering. The U-series isotopes are a geochemical tool to quantify rates of regolith formation and, therefore, can provide weathering rates of silicate minerals. In turn, this information can lead to a better understanding of the dynamics controlling the C-cycle and the climate over geological timescales.

1.3 Weathering profiles and regolith production rates

To assess the influence of chemical weathering processes on climate (e.g. CO$_2$ consumption) it is important to understand how these mechanisms operate. This thesis aims at studying chemical weathering occurring in regolith profiles. This section provides a brief overview of regolith processes of formation and characteristic. Particular attention is payed to rates of regolith formation.

1.3.1 The development of regolith profiles

The starting point for the formation of a regolith profile is the parent rock material (e.g. rock or sediments). Weathering is classified into two, interdependent categories: physical
and chemical. Physical weathering consists in the breaking up of the rocks by processes such as exfoliation, wedging and grinding. Chemical weathering consists in the decomposition of rock-forming minerals by reactions such as hydrolysis, carbonation and oxidation.

The formation of regolith can be conceptually described as a progressive downward movement of the weathering front from the surface into the bedrock (Figure 1.3). During this process, the profile gradually weathers and evolves in different horizons. Simultaneously, it supplies fresh material to weathering.

![Figure 1.3. Illustration of the progressive downward movement of the weathering front.](image)

The time required to develop a regolith varies from tens to millions of years, depending on several factors that affect weathering processes, i.e. i) lithology, ii) climate, iii)
biological activity, iv) relief and v) time (Byers et al., 1938; Targulian and Krasilnikov, 2007).

Lithology, or parent material, is an important factor as it supplies minerals to weathering. When the weathering front breaks down an intact parent material, the different minerals show different dissolution rates: very labile minerals such as anorthite and fosterite, show faster dissolution rates compared to more resistant minerals, such as quartz. For instance, Lasaga et al. (1994) reviewed the time required (i.e. lifetime) by different minerals to dissolve under laboratory conditions; these values are reported in Figure 1.4.

![Figure 1.4. Average lifetime for different minerals. These values represent the time required to dissolve crystals of 1 mm of diameter at 25°C and pH of 5 (compiled from Lasaga et al., 1994).](image)

Climatic factors, such as the temperature, precipitations and wind, affect regolith formation. Temperature and precipitation directly affect the rate of weathering: for instance, higher temperatures and greater rainfall generally increase weathering rates (Brady and Carroll, 1994; Stewart et al., 2001). Rainfall often plays a major role in the
re-distribution of components and elements among different regolith horizons, and influences the formation of soil types (Byers et al., 1938). Wind affects regolith development as it is a drying agent, introduces allochthonous material via dust deposition and removes regolith components by erosion (Verheijen et al., 2009).

Biological activity is another fundamental factor that influences regolith formation, as soil contains organic matter. Organic matter includes plants, microorganisms and any other biological products. The main functions of biological activity are to i) decay complex organic material such as dead plants and carcasses, ii) transport nutrients and water from the deeper horizons to the upper ones through plants roots, and iii) affect regolith texture (e.g. porosity) by bioturbation. For instance, plants grow their biomass, deepen their roots in regolith, transport water and nutrients through the profile and during these processes they physically mix the regolith. These processes also provide secondary functions; the decay of organic matter by microorganism produces organic acids, which, in turn, increase weathering and leaching processes (Lucas, 2001).

Relief is additional, important factor affecting pedogenic processes because it controls water availability (e.g. drainage, rain adsorption and other water-related processes) and erosion. As it was previously discussed, the presence of water is fundamental for weathering processes; relief spatially controls the availability of water. For instance, in an area with homogeneous lithology and precipitations, small variations in relief will concentrate water in depressions. The result is that in depressed areas soil will be more humid than on higher zones, affecting weathering processes and regolith development (Byers et al., 1938).

All the previous factors would not be effective without sufficient time. The factors operate together and, overall, their effects on regolith formation are integrated in time (Targulian and Krasilnikov, 2007). It is impossible to define a minimum period of time necessary to form a weathering profile. For instance, a sandy regolith developed under acidic conditions and humid climate may form faster (possibly in about few hundred years) compared to clayey profiles characterized by neutral pH and dry conditions (Byers et al., 1938). In such a case, the availability and mobility of the natural solution throughout the
profile would significantly influence the time required for weathering to occur and to develop the two profiles.

Lithology, climate, biological activity, relief and time interact together to form a weathering profile. These factors are interdependent and one modifies the effect of the other. For example, climate affects biological activity which in turn is modified by relief through drainage and run-off. The result of these complex mechanisms is regolith.

1.3.2 The regolith structure

During regolith development, weathering profiles differentiate due to diverse processes occurring at different depths, resulting in the formation of horizons. Regolith horizons can be classified in many ways; the simplest characterization of a regolith is its subdivision in soil and saprolite. The former is the upper layer, inhabited by organisms and plants, and that has lost the texture of the original bedrock. The latter is defined as a weathered rock that shows a texture similar to the bedrock. Alternatively, regolith can be divided as O, A, E, B and C horizons. The O horizon is the uppermost one and is chiefly made of organic matter. The A horizon mostly consists of resistant minerals (etc. clay, Fe-oxyhydroxide, quartz) and organic matter. The E horizon is also called *eluviated* because it has typically been heavily leached during regolith formation and is typically depleted in Fe, Al and organic matter. The B horizon, also referred to as *illuviated*, is the area in which the compounds leached from the other horizons are accumulated. Finally, the C horizon is the deepest one and coincides with the saprolite. It is defined as a slightly weathered parent material and below this horizon no pedogenic processes occur. In this thesis, the weathering profiles horizons will be described using these terms.

Regolith samples can be subdivided into four components: i) bedrock-derived phases, ii) solution-derived secondary phases, iii) organic matter and iv) aqueous solution (Figure 1.5). *Bedrock-derived phases* comprise both residual, primary minerals and secondary phases (e.g. clays) derived from incongruent dissolution of bedrock-forming minerals. *Solution-derived secondary phases* are precipitated from aqueous solution; e.g. precipitation of Fe-oxides, carbonates and clays precipitated from solution (Duff et al., 2002). Organic matter is produced by biological processes. Aqueous solution is typically soil pore water and can be derived from precipitations, groundwater or any other sources
of water. In this thesis, the ensemble of bedrock-derived phases, solution-derived secondary phases, organic matter and aqueous solution is referred to as bulk regolith. Note that bulk regolith samples are dried in an oven before any procedure; although the aqueous solution is removed from the sample by evaporation, the compounds dissolved in it remain in the sample (e.g. precipitate). This is because aqueous solution is regarded as a bulk regolith component.

All these components interact with each other and exchange material (e.g. chemical elements) via pedogenic processes (arrows in Figure 1.5). For example, when bedrock-derived phases interact with soil pore water, they may undergo incongruent (or congruent) dissolution. During the dissolution of olivine – (Mg, Fe)₂SiO₄ – the mobile Mg is easily removed from the mineral structure, while the less mobile Fe commonly recombines with SiO₂ to form clays. Depending on the weathering conditions, olivine dissolution results in the formation of smectite, montmorillonite, hematite and/or goethite (Delvigne et al., 1979). In other cases, elements dissolved in soil pore water may precipitate in the regolith; the formation of Fe-oxide and carbonates are an example (Duff et al., 2002).
1.3.3 Soil and regolith production rates

Gilbert and Dutton (1877) first studied soil production rates and associated them to the landscape evolution. In particular, they related soil production rate to soil depth – defined as the soil production function – and introduced the idea that the maximum rate of bedrock-soil conversion occurs under an optimal soil thickness.

The study of the soil production function remained very limited until the late 1960s and 1970s, when the interest for the soil production function was rediscovered by Ahnert (1967) and Armstrong (1976) (Humphreys and Wilkinson, 2007). The first study introduced a model to relate change in soil thickness per unit of time, $T$ (e.g. in mm/kyr), to three factors: i) regolith thickness added by bedrock weathering, per unit of time, $W$
(in mm/kyr), ii) rates at which sediment is added to the soil profile, \( S \) (in mm/kyr), for instance by lateral transport; and iii) rate of soil removal, \( R \) (in mm/kyr), e.g. erosion (Ahnert, 1967, 1994):

\[
T = W + S - R
\]  

(1)

Using this model, Ahnert (1967) showed that soil production rates decrease with increasing soil depth and suggested the presence of a defined soil thickness under which weathering rates are maximised. The thickness varies depending on several factors, such as lithology, climate and slope. Using a similar model, Armstrong (1976) concluded that on a hillslope, soils develop toward an equilibrium in which soil formation processes and erosion are equal. However, these studies did not quantify soil production rates.

Reneau et al. (1989) attempted to quantify the rates at which a bedrock is converted into regolith (referred to by the authors as bedrock lowering rates) on small hillslopes developed on tertiary sandstones and siltstones. This method is based on the assessment of rates of sediment accumulation and removal, using \(^{14}\text{C}\) chronology of deposited charcoal fragments. The study estimated an average bedrock lowering rate of 40 mm/kyr. In another work, Reneau and Dietrich (1991) applied the same method on hillslopes developed on Eocene greywacke sandstone and found an average bedrock lowering rates of 70 mm/kyr. A limitation of this method is that the \(^{14}\text{C}\) chronology cannot date systems older than \(\sim\)50 kyr, while soil can be much older (Hajdas, 2006).

Monaghan (1992) and McKean (1993) estimated in-situ soil production rates (referred to by the authors as bedrock-to-soil conversion rates) using meteoric cosmogenic \(^{10}\text{Be}\) in regolith developed on shale. This method is based on two mass-balance equations: first, an equation that describes the soil steady-state, i.e. rates of soil production and erosion are equal; and second, a model that defines the steady-state of \(^{10}\text{Be}\), i.e. \(^{10}\text{Be}\) input rate from the atmosphere equals the output rate by erosion (Monaghan et al., 1992). These studies reported soil production rates comprised between 115 and 270 mm/kyr (McKean et al., 1993; Monaghan et al., 1992). A limit of this method is that it requires a shorter residence time of soil material in the hillslope than \(^{10}\text{Be}\) residence time: in other words, \(^{10}\text{Be}\) mobilization has to be dominated by erosion or other mechanical processes, and not
by dissolution (e.g. in aqueous solution) or radioactive decay \( (T_{1/2} = 1.5 \text{ Myr}; \text{Monaghan et al., 1992}) \). Furthermore, this method requires the system to be in steady-state, a condition that is difficult to verify.

Heimsath et al. (1997) estimated soil production rates on eleven hillslopes developed on sandstone using in-situ produced cosmogenic isotopes \(^{10}\text{Be}\). This technique requires the measurement of \(^{10}\text{Be}\) concentrations in quartz grains separated from the bedrock (Heimsath et al., 1999). The soil production rates estimated using cosmogenic \(^{10}\text{Be}\) range between 15 to 107 mm/kyr (Heimsath et al., 1997). This method quantitatively demonstrated, for the first time, the soil production function, showing that soil production rates decrease with increasing soil thickness. The inverse relationship between soil production rates and soil depth has been later confirmed by several other studies by means of the cosmogenic isotopes (Heimsath et al., 2000; Heimsath et al., 2001; Heimsath et al., 1997; Heimsath et al., 1999; Larsen et al., 2014; Wilkinson et al., 2005). Humphreys and Wilkinson (2007) retraced the development of the soil production function in the last century and highlighted the importance that geochemical tools, such as the cosmogenic isotopes, have in order to understand and quantify the relationship between soil thickness and soil production rates.

Using in-situ cosmogenic isotopes, Dixon and von Blanckenburg (2012) and Larsen et al. (2014) investigated the relationship between soil production and tectonic uplift. This relationship is important because the uplift of the Tibetan plateau has been proposed to increase erosion rates and, consequently, global chemical weathering rates. The increase in chemical weathering rates may have decreased the atmospheric \( \text{CO}_2 \) concentration and produced the late Cenozoic cooling episode (Raymo and Ruddiman, 1992). Dixon and von Blanckenburg (2012) found that greater erosion rates produced by tectonic uplift do not increase chemical weathering and soil production rates. In contrast, Larsen et al. (2014) proposed that greater erosion rates produced by tectonic uplift result in greater soil production and chemical weathering rates, confirming the theory proposed by Raymo and Ruddiman (1992). Although these studies are contradictory, they are an example of the importance of quantifying soil and regolith production rates.
However, the cosmogenic isotope approach makes two main assumptions: steady-state soil thickness (i.e. soil production rate equals soil erosion) and constant soil bulk density. These assumptions limit the applicability of this technique. For instance, it is not always possible to verify the steady-state condition of soil thickness (Dosseto et al., 2008b). Moreover, this approach does not allow to assess whether, in a landscape, soil thickness is increasing or decreasing (Dosseto et al., 2008b).

Boulad et al. (1977) introduced an alternative approach for estimating rates of weathering and soil production using the uranium-series isotopes. These authors modelled the evolution of the \(^{230}\text{Th}/^{238}\text{U}\) activity ratios with depth in a lateritic profile in Cameroon and estimated a regolith production rate of 50 – 70 mm/kyr. The same approach was used by Mathieu et al. (1995), but it is only in the last 15 years, with the development of new analytical techniques such as the multi-collector inductively-coupled-plasma, that this approach was significantly developed (Chabaux et al., 2013; Dequincey et al., 2002; Dosseto et al., 2011; Dosseto et al., 2012; Dosseto et al., 2008b; Ma et al., 2010; Suresh et al., 2013). Regolith production rates inferred using U-series isotopes are discussed in details in the next section. This approach models the fractionation of the uranium-series isotopes with regolith depth, and obtains time information through their half-lives, which show timescales compatible with weathering processes. Dosseto et al. (2012) compiled regolith production rates estimated until then using uranium-series isotopes; the rates, calculated under various lithologies and climatic settings, showed values ranging between 10 and 334 mm/kyr. Compared to the previous methods, which assumed steady-state soil thickness, the uranium-series isotopes supply an independent means to assess regolith production rates. A fundamental requirement of this methodology is the understanding of the processes controlling the fractionation of the uranium-series isotopes during regolith development.

The present thesis focuses on the U-series isotopes approach. Our goal is to better understand the processes controlling U-series isotopes fractionation in regolith. This knowledge will be used to improve the accuracy of regolith production rates estimated using uranium-series isotopes.
1.4 Uranium-series at the Earth’s surface

Since the 1960’s, the uranium-series isotopes have been recognised as a potential tool to constrain time information of Earth’s surface processes such as regolith formation (Hansen and Stout, 1968; Rosholt et al., 1966). This is because U-series are composed by radioactive isotopes of several elements that fractionate during weathering processes. Moreover, their half-lives cover the timescale of common Earth’s surface processes.

This section summarizes the characteristics and mobility of radionuclides. The development of geochemical studies and methodologies increased from the 1980s’, when new technology made possible the measurement of concentrations and isotopic ratios on very small amounts of sample. Particularly, accurate measurements of U-series isotopic ratios are possible thanks to the progresses made in thermal ionization mass spectrometry (TIMS) and, more recently, in multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS).

The next sections summarize the mobility of the U-series radionuclides, the model used to estimate regolith production rates and the main results found in the literature.

1.4.1 The U-series isotope system and secular equilibrium

The parent nuclide $^{238}$U decays in a series of radioactive isotopes of different elements (e.g. U, Th and Ra), each of which is characterized by a different half-life ($t_{1/2}$; Figure 1.6). This study will focus on three nuclides: $^{238}$U ($t_{1/2} = 4.5$ Gyr), $^{234}$U ($t_{1/2} = 248$ kyr) and $^{230}$Th ($t_{1/2} = 75$ kyr).

The decay of a given number of atoms (N) was first described mathematically by Bateman (1910). For the parent nuclide $N_1$, the equation that describes its decay is:

$$\frac{dN_1}{dt} = -\lambda N_1$$

(2)

While for the intermediate nuclides $N_i$ in the decay chain (e.g. $^{234}$U) the equation is:
where $\lambda$ is the decay constant measured in yr$^{-1}$ ($\lambda = \ln2/t_{1/2}$) and $N_{i-1}$ is the number of atoms of parent nuclide of $N_i$. Instead of reporting the number of an atom present in a sample, the results of isotopic analyses are commonly reported as activities and activity ratios. The activity of a radionuclide is the number of disintegrations per unit of time (Bq) and is described mathematically as:

$$ (N_i) = N_i \lambda_i $$  \hspace{1cm} (4)

The activity ratio among two nuclides is calculated as:

$$ \frac{N_2}{N_1} = \frac{N_2 \lambda_2}{N_1 \lambda_1} $$  \hspace{1cm} (5)

A characteristic of radioactive systems is that, assuming a closed system, it is possible to calculate the variation of the number of nuclides ($N_i$) with time, as a result of radioactive decay (Bateman, 1910). This is described by the following equations (Bourdon et al., 2003):

$$ N_1 = N_1^0 e^{-\lambda_1 t} $$  \hspace{1cm} (6)

$$ N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} $$  \hspace{1cm} (7)

In this equations, $N_1^0$ and $N_2^0$ are the number of atoms at time zero and $t$ is the time elapsed (years). Because $\lambda_1 << \lambda_2$, if the two radionuclides $N_1$ and $N_2$ described in equation 7 remain in a closed system for a time greater than five or six times the half-life of the daughter nuclide $N_2$, the value of $(e^{-\lambda_2 t})$ get close to zero and $(e^{-\lambda_1 t})$ to one (Bourdon et al., 2003; Dosseto et al., 2008a). Equation 7 can be simplified as:

$$ N_2 \approx \frac{\lambda_1}{\lambda_2} N_1 $$  \hspace{1cm} (8)

Therefore,

$$ N_2 \lambda_2 \approx \lambda_1 N_1 $$  \hspace{1cm} (9)
In the case of the \(^{238}\text{U}\) and \(^{234}\text{U}\), this equation indicates that for a system that has remained closed for more than 1.2 Myr (~ five times the \(t_{1/2}\) of \(^{234}\text{U}\)), the activities of the daughter and parent nuclide will be equal and the \(\left(\frac{\text{234U}}{\text{238U}}\right)\) activity ratio will be equal to 1. This condition is known as secular equilibrium. For any activity ratio between two radioisotopes, the time required to reach secular equilibrium is approximately five times the \(t_{1/2}\) of the daughter nuclide. For instance, the \(\left(\frac{\text{230Th}}{\text{234U}}\right)\) needs to remain in a closed system for ~300 kyr to reach secular equilibrium. Because all the other intermediate radionuclides have half-lives shorter than that of \(^{234}\text{U}\), for a system that has remained closed for more than 1.2 Myr, all the activity ratios in the \(^{238}\text{U}\)-series will be in secular equilibrium, i.e. \(\left(\frac{\text{234U}}{\text{238U}}\right) = \left(\frac{\text{230Th}}{\text{238U}}\right) = 1\) (Cowart and Burnett, 1994).

Figure 1.6. The uranium-238 radioactive decay chain. The half-lives for each nuclide are reported below the isotope symbol. The grey boxes highlight the isotopes most commonly used in geochemical studies. Modified from Dosseto et al (2008a).
1.4.2 The starting point: bedrock and secular equilibrium

Uranium-series isotopes found in environmental compartments (i.e. soils, sediments, river water, ocean etc.) are derived from rocks. The interaction between rocks and the Earth’s surface results in the mobilization and subsequently, re-distribution of the U-series isotopes in environmental compartments through processes such as physical and chemical weathering. If a bedrock has remained in a closed system for more than 1.2 Myr, it is in secular equilibrium. This is confirmed by several studies which observed that unweathered rocks are in secular equilibrium (e.g. Dequincey et al., 1999; Dosseto et al., 2006b; Dosseto et al., 2008b; Pelt et al., 2013; Suresh et al., 2014).

1.4.3 U-series isotopes mobility

The isotopes in the U-series chain are characterized by different chemical mobility; thus, during weathering processes and their transfer to the environmental compartments they fractionate. This is showed by the radioactive disequilibrium that is commonly observed in soils, sediments and aqueous solutions (e.g. ground waters, rivers and oceans Chabaux et al., 2013; Chabaux et al., 2001; Chen et al., 1986; DePaolo et al., 2006; Dequincey et al., 2002; Dosseto et al., 2006a; Dosseto et al., 2006b; Martin et al., 2015; Pelt et al., 2013). Two main processes contribute to U-series isotope fractionation during weathering (Chabaux et al., 2003; Gascoyne, 1992). The first one is chemical fractionation due to different chemical properties of isotopes of different elements. For instance, U isotopes are more soluble than Th isotopes. The second process is alpha recoil, which is produced by nuclear decay reactions. The integral of these two factors defines the mobility of a radionuclide during Earth’s surface processes.

Chemical fractionation

Chemical fractionation among isotopes of different elements (U and Th) is the result of differences in their chemical properties. Many notable reviews of the aqueous chemistry of U and Th are available in the literature (e.g. Allard et al., 1984; Bourdon et al., 2003; Chabaux et al., 2003; Murphy and Shock, 1999). The main environmental factors that control the U-Th fractionation are thermodynamic parameters, such as pressure and temperature, and solution composition (pH, ionic strength, redox potential). Moreover, U
and Th interact differently with minerals and organic matter. This section summarizes the major factors controlling chemical fractionation of these two elements.

**Uranium**

In solution and under common environmental conditions, U shows two oxidation states: U$^{4+}$ and U$^{6+}$ (Figure 1.7). Uranium (4+) forms under reducing conditions and is nearly immobile, as it precipitates as the mineral uranite (UO$_2$). Its mobility increases at low pH and in the presence of ligands such as fluorides. Most of the mobile U in the environment is in the 6+ oxidation state, which is formed under oxidising conditions (e.g. at the Earth’s surface). In solution, U$^{6+}$ forms uranyl ions (UO$_2^{2+}$), which complex with several ligands that are commonly found in natural solution (Figure 1.8). For instance, at pH lower than 4, U is commonly present in solution as uranyl ion and uranyl fluoride (UO$_2F^+$), while at pH greater than 8, U combines with carbonate species (Langmuir, 1978).

Once U is dissolved in natural solution it may interact with minerals and organic matter. These interactions are mainly controlled by two factors: i) mineral type and ii) physico-chemical properties of the aqueous solution. Dissolved U can be adsorbed onto mineral surface; for instance, clay minerals, Fe-oxides and micas are well known to uptake U from solution (Ames et al., 1983a; Ames et al., 1983b). Uranium is adsorbed onto mineral grains via complexation of dissolved, positively charged U species, such as UO$_2^{2+}$, and negatively charged mineral sites, such as FeO$^-$ (Read et al., 1993; Sims et al., 1996). Amorphous Fe- oxyhydroxides are particularly efficient in adsorbing U when compared to crystalline, secondary phases such as illite and montmorillonite (Ames et al., 1983a; Pett-Ridge et al., 2007). The adsorption of U onto minerals is also affected by physico-chemical characteristics of the aqueous solution. For instance, pH plays an important role in U adsorption onto minerals: maximum uptake generally occurs at nearly-neutral pH (Pabalan et al., 1998). Temperature is another factor playing an important role; U adsorption onto minerals decreases with increasing temperature (Ames et al., 1983a). As a result, the interaction of U in solution and minerals may significantly decreases U mobility in the environment (Duff et al., 2002).
Uranium has strong affinity for organic matter; this has a dual effect on U mobility in natural water. On the one hand, soluble organic ligands (e.g. humic acids) increase the mobility of U in aqueous solution (Lenhart et al., 2000). On the other hand, the presence of insoluble organic ligands in the regolith adsorbs U and reduces its mobility (Murphy et al., 1999; Zielinski and Meier, 1988).

Chabaux et al. (2003) highlighted two important characteristics of U mobility in the environment. Firstly, U mobility may be reduced by interactions with minerals and inorganic/organic ligands. For instance, pH can greatly affect the mobility of U in soil: for pH > 5 dissolved U is precipitated in or adsorbed onto solid soil components (Abdelouas et al., 1998; Crançon et al., 2010; Crançon and Van der Lee, 2003; Del Nero et al., 1999). Secondly, U immobilization due to interactions with minerals and/or ligands is reversible, as these processes are affected by variations in physico-chemical conditions of the environment. For example, a decrease in the pH of soil pore water may result in the re-mobilization of U previously precipitated onto soil grains. Additional factors that may re-mobilize U adsorbed onto soil mineral are the presence of dissolve organic and/or inorganic ligands and variations in water ionic-strength, temperature and redox potential (Crançon et al., 2010; Crançon and Van der Lee, 2003).
Figure 1.7. Fields of stability for the most common U species as a function of pH and oxidation-reduction potential at 25 °C. Reprinted from Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits; Langmuir (1978), Geochimica Cosmochimica Acta, Vol. 42, Fig 2, p. 554 (with permission of Elsevier, copyright 1978).
Thorium

Thorium is commonly present in the Th$^{4+}$ oxidation state, which is mostly immobile. However, its mobility significantly increases at pH < 4; for instance, the mineral thorianite (ThO$_2$) is soluble only in very acidic conditions. Similarly to U, Th has a high affinity for inorganic ligands, in particular fluoride, phosphate, hydroxide and sulfate, which increase its mobility especially at pH between 2 and 8 (Figure 1.10). A similar effect is observed in presence of organic ligands, such as humic acids (Langmuir and Herman, 1980).

Once dissolved in solution, Th can interact with minerals, such as clays and Fe-oxides, and be adsorbed onto their surface (Langmuir and Herman, 1980; Syed, 1999). Compared to U, Th has a stronger affinity for organic matter. On the one hand, this increases Th
mobility; in fact, most of Th dissolved in natural water is associated with organic ligands (Langmuir and Herman, 1980). On the other hand, Th can be adsorbed onto solid organic matter (Crançon et al., 2010; Langmuir and Herman, 1980). These two processes compete for Th, and similarly to what Chabaux et al. (2003) pointed out for U, Th immobilization has to be considered a reversible process.

Figure 1.9. Relative concentration in solution of Th complexed with different inorganic ligands, plotted against pH and at 25 °C. Reprinted from *The mobility of thorium in natural water at low temperature*; Langmuir and Herman (1980), Geochimica Cosmochimica Acta, Vol. 44, Fig 7, p. 1761 (with permission of Elsevier, copyright 1980).
Figure 1.10. Solubility of thorianite versus pH in pure water and in presence of organic and inorganic ligands, and at 25 ºC. Reprinted from The mobility of thorium in natural water at low temperature; Langmuir and Herman (1980), Geochimica Cosmochimica Acta, Vol. 44, Fig 11, p. 1763 (with permission of Elsevier, copyright 1980).

*Alpha-recoil*

The second process that fractionates U-series isotopes is alpha recoil. The alpha decay of a parent nuclide produces a daughter nuclide, an alpha particle and energy. In a solid material, like in the crystal lattice of a rock-forming mineral, the energy produced displaces the daughter nuclide by more than 20 nm (referred to as alpha-recoil range; Kigoshi, 1971). The displacement is referred to as alpha-recoil. This increases the daughter-nuclide mobility via two main mechanisms: i) preferential leaching and ii) direct ejection of the radiogenic isotope.

Preferential leaching occurs when the parent nuclide, located in the mineral lattice, decays, the energy released displaces the daughter nuclide and produces alpha-recoil.
tracks. The daughter nuclide will be located in an alpha-recoil track, which is a damaged region of a mineral crystal lattice from which the aqueous solution can easily remove the nuclide during mineral dissolution (Gögen and Wagner, 2000; Murakami et al., 1991). During weathering of the mineral grain, the daughter isotope is preferentially mobilized relative to its parent, which is located in a more stable location of the crystal lattice (Kigoshi, 1971). Alpha-recoil tracks are also produced by ejection of nuclides from a mineral (donor) directly into an adjacent grain (recipient), where it is embedded. This process occurs when two minerals are adjacent, no solution is present between the grains (as the alpha-recoil range for the ejected nuclide in air is longer than in water) and the parent nuclide is sufficiently close to the donor-mineral surface to eject the daughter nuclide directly in the recipient (Fleischer, 1980).

The radiogenic isotope can also be directly ejected outside a mineral grain. In this case, the parent nuclide needs to be located close to the mineral surface (i.e. less than ~55 nm). This process was first demonstrated by Kigoshi (1971), who studied the decay of $^{238}$U in zircon powder and the direct ejection of its daughter, $^{234}$Th, into surrounding water. Kigoshi (1971) also described mathematically $Q$, the rate of direct ejection of $^{234}$Th in solution by alpha decay:

$$Q = \frac{1}{4} LS u \rho \lambda$$

where $L$ is the distance at which $^{234}$Th is recoiled (alpha-recoil range; measured in nm), $S$ is the surface area of mineral grains (cm$^2$), $\rho$ is the mineral density (g/cm$^2$), while $u$ and $\lambda$ are the concentration of $^{238}$U in the mineral (ppm) and the decay constant of $^{238}$U (yr$^{-1}$), respectively. By measuring the amount of $^{234}$Th released in solution by zircon powder, Kigoshi (1971) used Equation 10 to calculate an alpha-recoil range ($L$) of about 55 nm. This study concluded that the direct ejection of $^{234}$Th into water explains the ($^{234}$U/$^{238}$U) activity ratios greater than 1 observed in natural waters (Andersen et al., 2009a; Borole et al., 1982; Osmond and Ivanovich, 1992; Somayajulu and Goldberg, 1966).

Another processes playing a role in the fractionation of the U-series isotopes was proposed by Sheng and Kuroda (1984). These authors observed that fine-grained minerals can eject and implant $^{234}$Th (hence $^{234}$U) from a grain to another. In particular, when one
mineral is U-rich and the other is U*-poor, this process results in the U-poor mineral enriched in $^{234}\text{Th}$ and $^{234}\text{U}$ relative to $^{238}\text{U}$. In contrast, the U-rich mineral will be depleted in the daughter nuclides. If the solubility of the U-rich mineral is greater than the U-poor mineral, during weathering the U-rich will dissolve leaving the solid residue enriched in the U-poor mineral and, therefore, with $(^{234}\text{U} / ^{238}\text{U})$ activity ratio $> 1$. For example, this can be the case of a rock containing apatite, which is labile and U-rich, and quartz, which is resistant to weathering and depleted in U. This mechanism can be referred to as Sheng-Kuroda effect (Bogdanov et al., 2011).

Many works have studied the U-series isotopic composition of the ocean, rivers and regolith, and hypothesised that the expected mobility of the U-series isotopes in the environment is $^{234}\text{U} > ^{234}\text{U} > ^{230}\text{Th}$ (e.g. Andersen et al., 2013; Chabaux et al., 2008; Chabaux et al., 2003; Dosseto et al., 2008b; Ku et al., 1977; Rosholt, 1982; Zielinski and Rosholt, 1978). Ku et al. (1977) analysed the U-series isotopic composition of 63 seawater samples collected from the Antarctic, Atlantic, Pacific and Arctic oceans and found an average $(^{234}\text{U} / ^{238}\text{U})$ of 1.14 ± 0.03. Other studies have measured the isotopic composition of river waters and found $(^{234}\text{U} / ^{238}\text{U}) > 1$: for instance, Plater et al. (1992) analysed the composition of river water in U.K. and found $(^{234}\text{U} / ^{238}\text{U})$ ranging between $1.197 ± 0.077$ and $1.333 ± 0.102$. Andersen et al. (2013) made a global compilation of the $(^{234}\text{U} / ^{238}\text{U})$ of main rivers and found an average activity ratio of $~1.24$. Activity ratios greater than one were also observed in river water by Dosseto et al. (2008a) in the Amazon basin. In contrast to river and ocean water, regolith is expected to be depleted in the more mobile $^{234}\text{U}$ relative to $^{238}\text{U}$ and, hence, show $(^{234}\text{U} / ^{238}\text{U}) < 1$; this was observed by several studies (e.g. Chabaux et al., 2003; Dosseto et al., 2008a; Dosseto et al., 2008b; Suresh et al., 2013).

Some laboratory experiments have shown that the mobility of the U-series isotopes does not always follow the pattern hypothesised by the above studies. In a laboratory experiment, Andersen et al. (2009a) leached a granitic rock for 1100 hr and analysed the $(^{234}\text{U} / ^{238}\text{U})$ activity ratios of the leachates. In the first part of the experiment, the authors found a continuous decrease in U concentrations with time associated with $(^{234}\text{U} / ^{238}\text{U})$ activity ratios greater than 1; this implies preferential mobilization of $^{234}\text{U}$ relative to $^{238}\text{U}$,
as expected. During the second part of the experiment, the leachates showed \((^{234}\text{U}/^{238}\text{U})\) lower than unity, implying that during this period \(^{238}\text{U}\) was preferentially mobilized compared to \(^{234}\text{U}\). This contrasts with the nuclide mobility proposed by other studies. To explain this behaviour, the authors hypothesised that the rock contains a pool of readily leachable \(^{234}\text{U}\), likely located in damaged sites of the mineral lattice. This pool is released in solution during the initial part of the experiment and produces a leachate with \((^{234}\text{U}/^{238}\text{U}) > 1\). When this pool terminates, the residual rock is depleted in \(^{234}\text{U}\) relative to \(^{238}\text{U}\); additional leaching released in solution \(^{234}\text{U}\) with \((^{234}\text{U}/^{238}\text{U}) < 1\), resulting in leachates with \((^{234}\text{U}/^{238}\text{U}) < 1\).

In a similar experimental setting, Bonotto and Andrews (2000) leached and etched samples of dolomite and limestone. In the case of the dolomite, the leaching and etching solutions showed \((^{234}\text{U}/^{238}\text{U}) > 1\), indicating preferential mobilization of the radiogenic isotope. In contrast, during the leaching and etching of a limestone sample, the activity ratios of the leaching and etching solutions were lower than unity, indicating preferential mobilization of \(^{238}\text{U}\) relative to \(^{234}\text{U}\). The explanation provided by the authors was that the limestone sample contained a micaceous mineral depleted in \(^{234}\text{U}\) relative to \(^{238}\text{U}\) and that the dissolution of this mineral during the experiment resulted in the leaching and etching solutions characterized by \((^{234}\text{U}/^{238}\text{U}) < 1\). They also hypothesised that the micaceous mineral has been depleted in \(^{234}\text{U}\) over \(^{238}\text{U}\) by weathering processes occurred before the experiment (the limestone sample was collected from a quarry stockpile). The studies by Andersen et al. (2009a) and Bonotto and Andrews (2000) suggest that the expected mobility of the U-series isotopes is not always shown during weathering and that our current knowledge on the nuclides mobility is quite limited.

During pedogenesis, the presence of primary and secondary minerals, and of organic matter in regolith affects the mobility of the U-series isotopes (Chabaux et al., 2003). The nuclide mobility in regolith may result difficult to explain with simple chemical fractionation and alpha-recoil processes. The behaviour of the U-series isotopes in regolith is discussed in the following section.
1.4.4 U-series isotopes in regolith components

The redistribution of the U-series isotopes in weathering profiles is mostly controlled by i) their location in the bedrock-forming minerals, ii) organic matter and secondary phases present in the regolith, iii) the presence of ligands in solution and iv) the external addition of U and Th, for instance via aqueous solution (Chabaux et al., 2003; Rosholt et al., 1966). The location of U and Th in bedrock-forming minerals is fundamental, as if they are located in resistant minerals (e.g. zirconium), they will not be taken up in solution. For example, Moreira-Nordemann (1980) showed that more than 60% of U contained in a soil collected from the Preto River basin was contained in resistant, heavy minerals such as zircon and monazite and is not significantly mobilized by weathering processes. The presence of ligands, secondary phases and clays can increase and decrease the mobility of U and Th throughout a profile (Duff and Amrhein, 1996; Duff et al., 2002).

The first studies focusing on the U and Th fractionation during pedogenesis were carried out during the 1960s and highlighted that regolith is commonly enriched in U and Th relative to the parent material (e.g. Hansen and Stout, 1968; Moreira-Nordemann and Sieffermann, 1979; Rosholt et al., 1966). Hansen and Stout (1968) explained that U and Th are less mobile during pedogenesis compared to other elements such as Mg and Ca, resulting in soils enriched in U and Th relative to the parent material. The same authors observed that U is mostly concentrated in the A horizon compared to the other horizons, while Th is leached and concentrated in the B horizon, often in association with organic matter (Hansen and Huntington, 1969). Similar results were observed by Greeman et al. (1990) in soils developed over carbonate bedrock from Pennsylvania. The soils showed U concentration 10 to 12 times higher than in the bedrock, while Th concentrations were 20 times greater. These profiles showed A-horizons depleted in U and Th when compared to deeper soil horizons; U and Th were eluviated from the A-horizon and illuviated deeper in the B-horizon. A contrasting U and Th migration pattern was showed by Rosholt et al. (1966): in a soil characterized by organic-rich A horizon, the authors hypothesised an upward movements of U through capillarity of soil pore water.

Secondary phases and organic matter play a major role in the migration and redistribution of U and Th in regolith. For instance, Greeman et al. (1990) found that both U and Th
(along with other elements such as Fe) were leached from the upper part of the profile and immobilized deeper. The greater U and Th concentrations in deeper soils were related to the presence of clay minerals, particularly Fe-oxides, which were more concentrated in the deeper part of the profiles. In this case, the U migration can be explained as mobilization of U from the upper part of the profile, along with other elements such as Fe, and immobilization in the deeper part due, for example, to co-precipitation of U with Fe-oxides (Abdelouas et al., 1998; Duff et al., 2002). It is possible that in certain regolith profiles U in the upper horizon cannot be easily mobilized. In a soil lixiviation experiment, Moreira-Nordemann and Sieffermann (1979) showed that rainwater enriched in organic matter mobilizes little U from soils. This suggests that in the studied soil U is located in resistant phases (e.g. heavy minerals and clays) and is not easily mobilized during weathering. In regolith profiles, Th is mobilized mostly by its complexation with organic and inorganic ligands (Chabaux et al., 2003). The study by Rihs et al. (2011) provides an example: in a podzol, the authors observed Th migration from the upper to the lower part of the soil profile and explained that Th is complexed by organic ligands in the upper part of the profile, leached downward in the B horizon and immobilized in this area.

External addition of U and Th due, for instance, to dust deposition can significantly affect the budget of U and Th in a regolith. This was shown by Pelt et al. (2013), who studied the influence of dust in two soils from the Mount Cameroon volcano and found that dust deposition can represent up to 25% of the U and Th present in the soils. In a chronosequence of soils from Hawaii, Pett-Ridge et al. (2007) reported increasing gains of U caused by dust deposition with increasing soil age, highlighting the importance of dust deposition on soil U budget. Although we understand the chemical properties of U and Th, their mobilization in the environment remains difficult to model and comprehend because of the numerous interactions between these elements and other environmental components.

During pedogenesis, the different regolith components are expected to exchange U-series isotopes (e.g. Dequincey et al., 2002; Pliler and Adams, 1962; Rosholt et al., 1966). In section 1.3.3 a representation of the different regolith components of a weathering profile was introduced (Figure 1.5).
Figure 1.11 shows the same representation and proposes the expected U-series isotopic composition for each regolith component. The bedrock is in secular equilibrium, while the expected isotopic compositions of bedrock-derived phases is ($^{234}\text{U}/^{238}\text{U}$) <1 and ($^{230}\text{Th}/^{238}\text{U}$) >1, as they are the products of bedrock weathering (Latham and Schwarcz, 1987). In contrast, solution-derived secondary phases, organic matter and aqueous solution are enriched in the more mobile isotopes and, therefore, are expected to show ($^{234}\text{U}/^{238}\text{U}$) >1 and ($^{230}\text{Th}/^{238}\text{U}$) <1 (Andersen et al., 2009a; Chabaux et al., 2008; Chabaux et al., 2011; Dosseto et al., 2008b). In each horizon, the U-series isotopic composition of the bulk material will reflect the composition of the dominating component(s) (Moreira-Nordemann and Sieffermann, 1979).

An example of a regolith dominated by removal of U-series isotopes due to water-rock interaction is the study by Ma et al. (2013). The authors found ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios that decreased and increased respectively with decreasing depth, reflecting the U-series nuclides mobility ($^{234}\text{U} > ^{238}\text{U} > ^{230}\text{Th}$). The observed isotopic ratios reflect the composition expected from weathering products (i.e. bedrock-derived phases). In such a case the isotopic composition of the bulk regolith is dominated by the composition of bedrock-derived phases (which is expected to be ($^{234}\text{U}/^{238}\text{U}$) <1 and ($^{230}\text{Th}/^{238}\text{U}$) >1).

A contrasting example is reported by Andersen et al. (2013), who studied the behaviour of U-series isotopes in six soil profiles developed over an alluvial area in Glen Feshie, Scotland. The soils showed ($^{234}\text{U}/^{238}\text{U}$) both greater and lower than 1; the authors hypothesised that the observed isotopic compositions are the result of U addition and removal, respectively. The addition of U was related to flood events, in which U contained in river water, which is characterized by an average ($^{234}\text{U}/^{238}\text{U}$) of 1.7, has been introduced and adsorbed onto soil components. This results in soil characterized by ($^{234}\text{U}/^{238}\text{U}$) >1. In contrast, removal of U enriched in $^{234}$U relative to $^{238}$U by weathering resulted in soil showing ($^{234}\text{U}/^{238}\text{U}$) <1. Preferential mobilization of $^{234}$U over $^{238}$U was related to direct ejection of $^{234}$U outside mineral grains by alpha-recoil and to preferential leaching of $^{234}$U located in damaged sites of mineral crystal lattices.

Since the first studies of the U-series isotopic composition of weathering profiles, researchers recognised the potential of this isotopic system as a geochemical tool to assess
regolith production rates (Rosholt et al., 1966). However, only later and particularly in the last 15 years, methods to model the U-series isotopic composition of weathering profiles and to estimate regolith production rates were applied. In the following section the development of the method to estimate regolith production rate is reviewed.

1.4.5 The development of the model to estimate regolith production rates.

The evolution of the U-series isotopic composition with regolith depth can be modelled to estimate rates of regolith production. To do this, the time elapsed since the onset of bedrock weathering is calculated by modelling the U-series isotopic composition of the weathering profile, this information is then converted in regolith production rates (commonly expressed in mm/kyr) using the profile depth. The first regolith production rates estimated using the U-series isotopes were proposed by Boulad et al. (1977). These
authors considered only the \( ^{230}\text{Th}^{/^{238}\text{U}} \) activity ratio and assumed that radioactive disequilibrium in the regolith was mainly produced by two processes: i) continuous U loss with decreasing depth and ii) leaching of U from the upper part of the profile and illuviation in the central area of the profile. Additional assumptions were that Th is immobile and U gain and loss is described by first kinetic reactions. The modelling of the \( ^{230}\text{Th}^{/^{238}\text{U}} \) variation with depth estimated a regolith production rate of 50-70 mm/kyr.

Latham and Schwarcz (1987) suggested a model to estimate rates of U-series isotopes removal from crystalline rocks during weathering. This model assumes continuous loss of U-series isotopes since inception of the bedrock weathering and that \(^{230}\text{Th}\) is immobile. The evolution in time of the abundance of the radionuclide \( j \) \((N_j)\) is described as follows:

\[
\frac{dN_j}{dt} = \lambda_i N_i - \lambda_j N_j - c_j N_j
\]

where \( t \) is time (yr), \( N_i \) is the abundance of the parent nuclide \( i \) (number of atoms), \( \lambda_i \) and \( \lambda_j \) are the decay constants for \( i \) and \( j \) (yr\(^{-1}\)), and \( c_j \) is the leach constant for \( j \) (yr\(^{-1}\)). The constant \( c_j \) represents the loss of nuclide \( j \) as a result of chemical leaching. Assuming that weathering continuously removes \(^{238}\text{U}\) and \(^{234}\text{U}\), the activity of \(^{238}\text{U}\) and \(^{234}\text{U}\) will decrease relative to the activity of \(^{230}\text{Th}\). This implies the presence of a certain amount of \(^{230}\text{Th}\) unsupported by its parent isotopes \(^{238}\text{U}\) and \(^{234}\text{U}\). Using the \(^{230}\text{Th}\) decay constant, the model estimates the rate at which \(^{238}\text{U}\) and \(^{234}\text{U}\) have been removed from the system. Because \(^{230}\text{Th}\) mobilization can occur during regolith formation, this model is limited to cases where the bedrock is only slightly weathered (Latham and Schwarcz, 1987; Pliler and Adams, 1962).

Scott et al. (1992) proposed two models to describe the evolution of the U-series isotopic composition during rocks weathering. The first model is equivalent to the one introduced by Latham and Schwarcz (1987) and is based on continuous removal of U-series isotopes. The second model is based on continuous addition of nuclides to the rock during rock-water interaction and was described as follows:

\[
\frac{dN_j}{dt} = \lambda_i N_i - \lambda_j N_j + k_j
\]
where $\lambda_i, N_i, \lambda_j, and N_j$ have the same meaning of the previous equation, while $k_j$ represents the addition of nuclide $j$ supplied by an external source at a constant rate ($\text{yr}^{-1}$).

More recently, an alternative model to describe the evolution of the U-series isotopes during the formation of a weathering profile was proposed by Dequincey et al. (2002) and later modified by Dosseto et al. (2008b). In this model, the U-series isotopic composition of a regolith sample continuously evolves from the moment in which its components began weathering in the bedrock and during regolith development, as a result of three factors. First, continuous loss of U-series isotopes, represented by the coefficient $k_j$, via chemical weathering (e.g. dissolution of bedrock-derived phases). Second, continuous uptake of U-series isotopes, represented by the coefficient $f_j$, due to precipitation of solution-derived secondary phases (e.g. illuviation), organic matter and/or other U-Th inputs such as dust deposition. Third, the time elapsed since the onset of bedrock weathering. The model assesses the evolution with time of the ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios of a sample, from the moment in which fractionation (thus weathering) begins in the bedrock until the sample is collected (Figure 1.12). The variation in time of the abundance of the nuclide $j$ ($N_j$) is:

$$\frac{dN_j}{dt} = \lambda_i N_i - \lambda_j N_j + f_j N_{j,0} - k_j N_j$$

(12)

where $t$ is time (yr), $\lambda_i$ and $\lambda_j$ are the decay constants (yr$^{-1}$) of the parent nuclide $i$ and its daughter $j$, $N_i$ is the number of the nuclide $i$ in the sample, $f_j$ is the uptake coefficient of the nuclide $j$ and $k_j$ is the loss coefficient for $j$. The terms $f_j$ and $k_j$ are coefficients that represent the rate, measured in yr$^{-1}$, at which $N_j$ is gained (uptake) and lost, respectively.
Figure 1.12. Graphical representation of the regolith production rate model. Initially, sample A is located in the bedrock, which in this case is in secular equilibrium. When the bedrock interacts with a solution, weathering starts and U-series isotopes are lost and/or gained (uptake) by sample A, resulting in isotopic fractionation. Assuming constant nuclide uptake, $f_j$, and loss, $k_j$, represented by the dashed lines, the model calculates the time required to modify the isotopic composition of sample A in bedrock into sample A in regolith. To do this, the U-series isotopic composition of the bedrock and of the saprolite need to be measured.

If one considers a sample collected from a regolith profile and applies the model to $^{238}$U, $^{234}$U and $^{230}$Th, the ($^{234}$U/$^{238}$U) and ($^{230}$Th/$^{238}$U) activity ratios will be a function of $f_{U238}$, $f_{U234}$, $f_{Th230}$, $k_{U238}$, $k_{U234}$, $k_{Th230}$ and the time since bedrock weathering started, i.e. regolith residence time ($T_{res}$).

Conceptually, the model estimates the evolution of the isotopic composition of a sample as it starts weathering in the bedrock (at the rock-saprolite boundary), migrates upward into the regolith (as a result of the weathering front downward movement) and until it is sampled, i.e. after the time $T_{res}$ (Figure 1.13). The coefficients $f_j$ and $k_j$ are assumed constant throughout the entire weathering profile and during $T_{res}$, although they may show different values for each nuclide. The coefficients $f_j$ and $k_j$ are estimated modelling the
variation of the measured isotopic compositions at different regolith depths. Using this model it is possible to calculate the set of \( T_{\text{res}} \) for each sample and the \( f_j \) and \( k_j \) coefficients for the entire weathering profile that best reproduce the measured isotopic compositions of the regolith profile. The model is solved by using a large-scale trust-region-reflective algorithm provided by Matlab\textsuperscript{TM}. This algorithm is described in details by Coleman and Li (1994; 1996) and is based on an interior-reflective Newton approach. The algorithm produces a population \((n > 1000)\) of possible solutions by defining \( n \) sets of \( f_j, k_j \) and \( T_{\text{res}} \) that minimize the squared differences between measured and modelled \((^{234}\text{U}/^{238}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\) activity ratios. The set closest to the median of the population of solutions is selected as the model solution. The standard error of the population is used to estimate the errors on \( f_j, k_j \) and \( T_{\text{res}} \).

An average regolith production rate is calculated using the distance between the weathering front (e.g. bedrock-saprolite front) and the sample \((d_{\text{samp}}; \text{measured in m})\):

![Figure 1.13. Schematic diagram representing the model that estimates regolith residence time \((T_{\text{res}})\). At \( t_0 \) the sample is in the bedrock. At \( t_1 \) the weathering front moves downward and sample 1 starts weathering. At \( t_{\text{sampling}} \) samples are collected. In the case of sample 1, the regolith residence time of sample 1 is represented as: \( T_{\text{res}} 1 = t_{\text{sampling}} - t_1. \)
The RPR (m/yr) represents an average over the distance between the current weathering front and the sample, and is a value integrated over $T_{res}$ (yr).

The model makes three main assumptions (Chabaux et al., 2011; Dosseto et al., 2012). Firstly, weathering processes proceed vertically and downward into the parent material (see section 1.31). Secondly, the uptake coefficient, $f_j$, and the loss coefficient, $k_j$, remain constant during the time of regolith formation and throughout the profile. Thirdly, $f_j$ and $k_j$ operate at similar time scales. The first assumption implies negligible removal and addition of regolith to the profile due, for instance, to later transportation and slope-movement (Dosseto et al., 2008b). This assumption can be fulfilled by collecting samples from flat-topped areas rather than on slopes; this would minimize the addition and removal of regolith due to lateral transportation and slope-movement. The assumption of constant $f_j$ and $k_j$ coefficients during weathering is common in chemical weathering studies (Chamberlain et al., 2005; Dosseto et al., 2014). Laboratory experiments have shown that $k_j$ coefficients remain constant during mineral weathering (Andersen et al., 2009a; Latham and Schwarcz, 1987; White and Brantley, 2003). For instance, Andersen et al. (2009a) showed that during a laboratory dissolution of a granitic rock, U-series nuclides are removed in solution at a constant rate, i.e. constant $k_j$ coefficient. Note that even if $f_j$ and $k_j$ coefficients were not constant during weathering, they would represent integrated estimates over the $T_{res}$ (Dosseto et al., 2014). The assumption of similar time scales over which $f_j$ and $k_j$ coefficients operate may not be always satisfied; however, this assumption is a necessary constrain to mathematically solve the model (Dosseto et al., 2012).

Keech et al. (2013) tested the assumption of constant U-series isotope loss ($k_j$ coefficient) during pedogenesis. This study was conducted by analysing the isotopic composition of four soil profiles formed over a chronosequence of alluvial terraces located along the Merced River, California. The authors assumed that the composition of the four profiles reflects the composition of the same soil at different ages: the young soil represents the initial phase of weathering, in which soil is slightly weathered, whereas older soils represent profiles that underwent more weathering. In this setting, the authors argue that

\[
Regolith \text{ production rate} = \frac{d_{samp}}{T_{res}}
\]  

(13)
the different profiles should display analogous $k_j$ coefficient. For each profile, the authors calculated the average isotopic composition. The average values were plotted against time, from the average isotopic composition of the youngest profile toward the oldest. The authors modelled the observed isotopic composition variation using two approaches: firstly, they used a constant $k_j$ coefficient and, secondly, they used an approach where the $k_j$ coefficient changed with time. By comparing the two approaches, they concluded that a two-stage model, in which the $k_j$ coefficient changes during pedogenesis, can explain the U-series isotopic variation throughout the chronosequence. The two-stage approach results in slower weathering timescales when compared to the more commonly used one-stage approach (Keech et al., 2013). However, two weak points are present in this study. Firstly, the average isotopic composition calculated for each weathering profile may not represent the profile. Averages were calculated, depending on which profile, using between 3 and 10 samples collected at different depths. Secondly, it is possible that soils developed in different locations of the chronosequence underwent different pedogenic processes; e.g. vegetation cycling or podzol-like redistribution of elements. Hence, the assumption that the soils composing the chronosequence represent the same soil at different ages may not be realistic. Although a model where $k_j$ coefficients vary with time may significantly improve the modelling of U-series isotopic composition evolution during pedogenesis, more studies are needed in order to define an adequate method.

A limit of the model used to estimate regolith production rates is that $f_j$ does not differentiate between gains of nuclides due to dust deposition and to precipitation of secondary phases. However, at least in the saprolite, which is not in direct contact with the atmosphere and where mechanical mixing is not significant, dust input is usually negligible (Dosseto et al., 2012).

1.4.6 Regolith production rates inferred from U-series isotopes

In the last twenty years, a number of studies have attempted to estimate regolith, soil and saprolite production rates using U-series isotopes. These studies have investigated the influence of i) climate, ii) lithology and iii) erosion rates on regolith production rates (Chabaux et al., 2013; Dequincey et al., 2002; Dosseto et al., 2011; Dosseto et al., 2012; Dosseto et al., 2008b; Gontier et al., 2015; Keech et al., 2013; Ma et al., 2010; Ma et al.,
In addition, regolith production rates inferred from the U-series isotopes have been used to verify steady-state conditions of soils under different spatial scales, i.e. weathering profile, hillslope and entire watershed (Chabaux et al., 2013; Dosseto et al., 2011; Ma et al., 2010; Ma et al., 2013).

By studying similar weathering profiles developed under different climates, it is possible to assess the influence of present climatic conditions on regolith production rates. For instance, three studies have estimated similar regolith production rates modelling the U-series isotopic composition of weathering profiles developed over granitic lithologies, different climates and with similar regolith depths (comprised between 15 and 25 m). Firstly, Mathieu et al. (1995) studied a lateritic profile in tropical Amazonia, Brazil, and calculated regolith production rates of ~50 mm/kyr. Secondly, in the tropical, dry Burkina Faso, Dequincey et al. (2002) estimated a minimum production rate of 50 mm/kyr. Lastly, Dosseto et al. (2008b) calculated regolith production rates comprised between 12 and 77 mm/kyr in a retreating escarpment in temperate Australia. Altogether, these results suggest that current climatic conditions may not significantly affect regolith production rates in landscapes characterized by thick regolith (Dosseto et al., 2008b).

Two studies by Dosseto et al. (2011; 2012) underscore the major role played by lithology in controlling regolith production rates. Dosseto et al. (2011) used the U-series isotopes to estimate regolith production rates in i) a granitic weathering profile in a plateau in southeastern Australia and ii) a regolith developed over volcaniclastic parent material in eastern Puerto Rico. The granitic weathering profile displayed rates comparable to other studies made on similar parent materials (12-77 mm/kyr; Dequincey et al., 2002; Dosseto et al., 2008b; Mathieu et al., 1995), while the profile in Puerto Rico showed much greater rates, of about 211 mm/kyr. In the same weathering profile in Puerto Rico, Dosseto et al. (2012) re-estimated regolith production rates and found a value of ~334 mm/kyr, confirming high rates at this location. To explain these results, Dosseto et al. (2011; 2012) made a compilation of regolith production rates estimated using U-series isotopes under different lithological settings and quantitatively showed that parent material plays a major role in controlling regolith production rates. Figure 1.14 shows that volcaniclastic lithologies produce regolith at faster rates than granitic and shale parent materials; more
studies are needed to confirm this hypothesis (Dosseto et al., 2012). Interestingly, regolith production rates assessed over granitic lithologies but under different climates show similar values. This may indicate that weathering profiles developed over granite are little influenced by climate (Dosseto et al., 2012).

Gontier et al., (2015) investigated the role of bedrock grain-size by comparing regolith production rates of two neighbouring weathering profiles developed over two facies of the same rock and characterized by different grain sizes, i.e. one finely grained and the other coarser. The rates resulted very similar – ranging between 1 and 3 mm/kyr – suggesting that parent material grain-size has little effect on regolith production rates. Instead, geomorphological settings, such as rate of physical erosion, may play a major role in controlling soil production rates at this site.

![Figure 1.14. Compilation of regolith production rates inferred using the U-series isotopes under different climatic and lithological settings. Regolith production rates are not directly related to climate. In contrast, weathering profiles developed over volcanoclastic lithologies show rates significantly higher compared to shale and granite bedrocks. Reprinted from Rapid regolith formation over volcanic bedrock and implications for landscape evolution; Dosseto et al. (2012), Earth and Planetary Science Letters, Vol. 337-338, Fig 7, p. 53 (with permission of Elsevier, copyright 2012).](image-url)
The importance of erosion as a factor controlling regolith production rates was well shown in two studies by Ma et al. (2010; 2013). In a hill in Pennsylvania, they estimated regolith production rates on the north- and south-facing sides. Regolith production rates estimated for the south-facing slope resulted greater than the ones calculated for the north-facing slope (~50 versus ~20 mm/kyr). The authors suggested two interpretations. Firstly, differences in soil physical conditions, such as temperature, moisture and evapotranspiration, may explain the higher production rates at the south-facing slope. Secondly, higher regolith production rates in the south-facing slope may be the result of greater erosion rates experienced by this location during the periglacial period occurred ~15 kyr ago. The authors suggested that, between the two possibilities, the second is likely more important, implying that erosion rates stimulate regolith production rates. This conclusion is consistent with the study by Gontier et al., (2015), who estimated regolith production rates as low as 1-3 mm/kyr in a profile developed over a granitic bedrock in a slowly-eroding region in France. Note that in the latter work it is possible that the combination of slowly-weathering granitic lithology and low erosion rates resulted in very slow regolith production rates.

Dosseto et al. (2011; 2012) used a worldwide compilation of regolith production rates, inferred via U-series isotopes, and erosion rates to quantitatively explain the occurrence of cratonic, soil-mantled and alpine landscapes (Figure 1.15). In cratonic areas, such as in the case of the studies carried in Burkina Faso and Brazil (Dequincey et al., 2002; Mathieu et al., 1995), regolith production rates are faster than erosion rates and result in a continuous increase in the regolith thickness. In soil-mantled landscapes, such as in the sites studied by Dosseto et al. (2008b) and Ma et al. (2010) regolith production and erosion are comparable, resulting in regolith profiles in steady-state. In contrast, regions characterized by little to no soil cover, such as landscapes dominated by landslides, are the result of slow regolith production rates and high erosion rates. Although regolith production rates have not been assessed for agricultural areas, erosion rates calculated in these environments are significantly greater than regolith production rates estimated using U-series isotopes in any other environment until now. This implies that agricultural soil resource is expected to inexorably decline as regolith production may not keep up with high erosion rates (Dosseto et al., 2012).
Soil production rates inferred from U-series nuclides have also been used to assess whether or not the regolith of an environment is in steady-state. For instance, in a hillslope in South-eastern Australia Dosseto et al. (2008b) verified the steady-state of the soil by comparing soil production rates to erosion rates estimated by Heimsath et al. (2000) using cosmogenic $^{10}$Be, at the same site. As erosion rate and soil production rate were comparable, the author inferred that at this location soil thickness is neither growing nor decreasing. Similarly, in a nearby region in Southeastern Australia, Suresh et al. (2013) reached the same conclusion by comparing two soil production rates estimated independently: the first calculated by the authors using the U-series isotopes (ranging between 10 and 24 mm/kyr) and the other inferred by Heimsath et al. (2001) using cosmogenic isotopes (between 10 to 50 mm/kyr). While the method based on the cosmogenic isotopes assumes that the soil is in steady-state, the U-series method does...
not. Because the inferred soil production rates were similar, the assumption of steady-state was verified. In contrast, using a similar method, Ma et al. (2010; 2013; discussed in more details above) studied regolith production rates on a hill developed on shale bedrock and found different regolith production rates and erosion rates. Consequently, they concluded that the study site is not in steady-state. At the same location, West et al. (2013) found regolith production rates nearly twice as fast as erosion rates (calculated using cosmogenic isotopes) implying that regolith thickness is increasing. Although the significant difference between regolith production rates and erosion rates, these two values were within uncertainty; therefore, it is still unclear whether the regolith at this location is thickening.

Chabaux et al. (2013) assessed the steady-state at the scale of a watershed (Rio Icacos watershed, Puerto Rico). The authors estimated regolith production rates in one regolith profile using the U-series isotopes and compared this value to weathering rates and erosion rates inferred for the whole watershed by other authors, using different approaches (e.g. Brown et al., 1995; Buss et al., 2008; McDowell and Asbury, 1994; Riebe et al., 2003; Turner et al., 2003; White et al., 1998). The regolith production rate inferred by Chabaux et al. (2013) was comparable to the average weathering and erosion rates observed by the other authors. Chabaux et al. (2013) argued that the rate of regolith production is relatively homogeneous in all the watershed and that the system may be in steady-state. To confirm this hypothesis more weathering profiles need to be studied.

Overall, all the studies mentioned above demonstrate that regolith production rates inferred from the U-series isotopes provide a geochemical tool to better understand landscape evolution processes.

### 1.4.7 Required developments and thesis outline

Dosseto et al. (2008b) defined two main issues to address in order to improve the accuracy of the model to estimate regolith production rates using the U-series isotopes. First, isolate bedrock-derived phases from regolith by removing solution-derived phases and organic matter. This removes the assumption of constant nuclide uptake during regolith development, represented by the \( f \) coefficient in equation 12. Moreover, the isolation of bedrock-derived phases will eliminate from equation 12 the assumption that U-series
isotopes gain and loss occur at similar timescales during pedogenesis. Ideally, the model will depend only on losses of U-series nuclides from bedrock-derived minerals. Second, it is necessary to infer the depth at the bedrock-saprolite boundary at which isotopic fractionation begins. In addition, even if bedrock-derived phases are isolated the isotopic composition of the sample will be complicated by the contribution of different phases to the U-series nuclides budget. When the U-series nuclide budget is controlled by one bedrock-derived phase the model may return robust results. As the number of phases contained in the sample increases the model will return less accurate information, which in turn will be more complex to interpret (Dosseto, 2015).

This thesis focuses on the isolation of bedrock-derived phases from bulk samples using physical (mineral separation) and chemical methods (sequential extraction). All the studies mentioned in section 1.4.5 analysed the U-series isotopic composition of bulk regolith; this implies that bedrock-derived minerals, solution-derived phases and organic matter were incorporated in the analysed samples. The model used to estimate regolith production rates is based on the reconstruction of the evolution of the isotopic composition of a weathering profile with depth. It assumes constant uptake and loss of U-series isotopes (i.e. $f$ and $k$ coefficients), which occur at similar timescales. The occurrence of nuclide gain (by precipitation of solution-derived phases and organic matter) and loss (due to mineral weathering) at a similar timescale may be unrealistic and could lead to uncertainties in the model (Dosseto et al., 2012). By isolating bedrock-derived phases, nuclide gained through formation of solution-derived phases and precipitation of organic matter in regolith are eliminated; this could simplify the model from which regolith production rates are inferred. This is because the assumption of similar timescale between loss of nuclide via mineral weathering and gain through precipitation of solution-derived phases and organic matter is no longer needed. Uranium-series analyses of bedrock-derived phases are expected to return more accurate regolith production rates when compared to analyses performed on bulk material.

A first attempt to isolate bedrock-derive phases was performed by Suresh et al. (2013). They analysed the U-series isotopic composition of two weathering profiles located in the Murrumbidgee River catchment and estimated regolith production rates. In addition, a
sequential extraction protocol was applied to one of the profiles in order to remove secondary phases, isolate primary minerals from the samples and, ultimately, increase regolith production rates accuracy. They found that the protocol does not significantly affect the calculated regolith production rates, although producing different loss and gain coefficients. In this study, sequential extraction did not change the sample mineralogy; this is because secondary phases were not present. A sample containing secondary phases may be more suitable to study the effect of sequential extraction on the U-series isotopic composition of regolith and, on regolith production rates.

The aims of this thesis are:

- *Provide a method to isolate bedrock-derived phases from the regolith.* This was performed by investigating the effect of two pre-treatments on regolith isotopic composition: sequential extraction and mineral separation. The first method has been designed to sequentially, chemically remove solution-derived secondary phases (e.g. Fe-oxides and carbonates) and organic matter (Tessier et al., 1979). The second method is mineral separation by handpicking. We focus on assessing whether the U-series isotopic composition of leached samples and mineral separates is affected by solution-derived phases and/or organic matter.

- *To better comprehend U-series isotope fractionation during regolith formation and in particular in bedrock-derived phases.* This was done by studying the distribution of U-series isotopes throughout weathering profiles and integrating mineralogical information and major element concentrations.

This thesis focuses on three weathering profiles developed over basalt, sandstone and granitic bedrocks in flat-topped areas in the Southern Highlands, Australia. The tertiary basalt has an age comprised between 45 and 53 My. It is characterized by olivine and plagioclase phenocrysts cemented into a matrix containing glass, pyroxene, K-feldspar and plagioclase. The regolith is classified as Kraznozemic (Chapter 2). The granitic profile develops on a Silurian bedrock (Gunning granite formation) mainly composed of quartz, plagioclase and biotite, and small contents of alkali feldspar. The regolith is
classified as red kandosol. In contrast, the sandstone is Permian and is composed mostly by quartz and minor concentrations of K-feldspar and plagioclase. The weathering profile is classified as a Podzol. Overall, these three lithologies give the opportunity to study U-series isotopes mobility and the effect of sequential extraction and mineral separation in different environmental settings.

In the second chapter, a Kraznozemic regolith developed over basalt is investigated. In this case, handpicking was not possible because of the fine-grained matrix of the bedrock. Sequential extraction, followed by mild HF/HCl etching, was applied to understand its effect on regolith U-series isotopic composition. In the third chapter, a granitic weathering profile is investigated. Sequential extraction and separation of quartz and biotite were applied, and the U-series isotopic composition of bulk and leached samples, and mineral separates were compared to understand whether these treatments improve the accuracy of regolith production rates. Similarly, the fourth chapter focuses on the effect of sequential extraction and minerals separation (quartz) on a podzol developed on sandstone bedrock.

Figure 1.16 Map of New South Wales and locations of the three study sites.
Note on sequential extraction procedures

Sequential extraction is a group of methods used to separate trace elements from different soil/sediment fractions, such as i) exchangeable, ii) acid-soluble, iii) reducible and iv) oxidisable (Tessier et al., 1979). These procedures are also applied to isolate bedrock-derived phases from soil (Bacon and Davidson, 2008; Gleyzes et al., 2002). Since their development in the late 1970s, several protocols have been proposed by different authors until the National Institute of Standards and Technology (NIST) recognized a standard protocol developed by Schultz et al. (1998). The sequential extraction method used in this thesis is based on the protocol proposed by this author; the detailed procedure is reported in Chapters 2, 3, 4 and 6.

Sequential extraction procedures present two main limitations. Firstly, they may incompletely remove target phases – e.g. solution-derived phases – (Bacon and Davidson, 2008; Gleyzes et al., 2002; Lee, 2009; Martin et al., 2015). To address this issue, Lee (2009) and Martin et al. (2015) showed that by monitoring the $^{234}\text{U}/^{238}\text{U}$ activity ratio of the residue of sequential extraction it is possible to obtain information on the completeness of target phases removal. Martin et al. (2015) showed that sequential extraction followed by mild HF/HCl etching can effectively remove target phases. Secondly, Gleyzes et al. (2002) and Bacon and Davidson (2008) reported that some metals removed by sequential extraction may be re-adsorbed from the reagent solution. This issue can be, at least partially, eliminated by using complexing agents such as sodium citrate (Martin et al., 2015).

Overall, sequential extraction is a suitable protocol to remove target phases and associated metals from soil; this was demonstrated by several works such as Tessier et al. (1979) Lee (2009) and Martin et al. (2015). However, because of the variability of the soil composition, it is difficult to define a methodology that has the same effect on any sample (Schultz et al. 1998). It is, therefore, reasonable to expect slightly different effects of sequential extraction on different types of soil.
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2 Assessing the effect of sequential extraction on the uranium-series isotopic composition of a basaltic weathering profile

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2.1 Abstract

Soil sustainability implies maintaining the balance between soil erosion and production. While it is known how to assess soil erosion, only recently we have been able to estimate rates of soil and saprolite (namely regolith) production using uranium-series isotopes. This method assesses the time elapsed since rock-forming primary minerals start fractionating the U-series isotopes. Because the regolith is an ensemble of residual primary minerals, secondary phases and organic matter, to obtain accurate estimates of regolith production rates it is important to isolate residual primary minerals. This can be achieved using sequential extraction and etching as pre-treatment methods. Here, we assess their effect on U-series isotopic composition and define a method to isolate residual primary minerals from regolith.

We applied sequential extraction to a basaltic bedrock, saprolite and soil and compared the U-series isotopic composition before and after the treatment. We also measured major elements concentrations and mineralogy.

The bedrock was in secular equilibrium and sequential extraction resulted in unchanged ($^{234}$U/$^{238}$U), while increased ($^{230}$Th/$^{238}$U). In contrast, etching resulted in increasing the ($^{234}$U/$^{238}$U) and ($^{230}$Th/$^{238}$U) activity ratios, which is attributed to the removal of primary minerals. Relative to the bedrock, the saprolite showed no changes in U and Th concentrations, and activity ratios. We hypothesise that during the conversion of the bedrock into saprolite the U and Th budgets remain unaffected. Moreover, major elements and mineralogical analysis suggest that during this process rock-forming minerals are converted into secondary phases (clays). During this conversion the U-series isotopes are not fractionated; therefore, their removal is not needed. Relative to the saprolite, the soil showed gains of U and Th, ($^{234}$U/$^{238}$U) >1 and ($^{230}$Th/$^{238}$U) <1. We hypothesise that secondary phases and organic matter were precipitated during saprolite-to-soil conversion. They were removed by sequential extraction, which resulted in a residue with ($^{234}$U/$^{238}$U) <1 and ($^{230}$Th/$^{238}$U) >1.

To remove the unwanted phases from the regolith and improve production rates estimated using U-series, we suggest analysing untreated bedrock and saprolite and leached soil.
2.2 Introduction

Uranium-series isotopes can be used to estimate rates of regolith production and study weathering processes. This is because intermediate daughter nuclides of the U-series system have an array of half-lives that cover timescales of weathering processes (Chabaux et al., 2013; Chabaux et al., 2003; Dequincey et al., 2002; Dosseto et al., 2011; Dosseto et al., 2012; Dosseto et al., 2008; Ma et al., 2010; Suresh et al., 2013). For a system that has remained closed for more than 1 Myr, all U-series isotopes will be in secular equilibrium (i.e. daughter-parent activity ratios will be 1). When the bedrock starts weathering and its primary minerals dissolve, U-series isotopes fractionate and the solid residue deviates from secular equilibrium. Once the disequilibrium is produced the U-series systems will tend to return to secular equilibrium through radioactive decay (Dosseto et al., 2008a). For instance, if a system remains closed following fractionation, the $^{234}\text{U}$ and $^{238}\text{U}$ pair will require ~1 Myr to re-establish secular equilibrium, while $^{230}\text{Th}$ and $^{234}\text{U}$ will take ~300 kyr. The fractionation of the U-series isotopes reflects the nuclide chemical mobility, which is uranium-234 ($^{234}\text{U}$) > uranium-238 ($^{238}\text{U}$) > thorium-230 ($^{230}\text{Th}$) (Chabaux et al., 2003). As a result, weathering products, such as residual primary minerals found in regolith, are expected to show ($^{234}\text{U}/^{238}\text{U}$) < 1 and ($^{230}\text{Th}/^{238}\text{U}$) > 1, where parenthesis denote activity ratios through this article. In contrast, the solution that weathers primary minerals – such as soil-pore water – will be characterized by ($^{234}\text{U}/^{238}\text{U}$) > 1 and ($^{230}\text{Th}/^{238}\text{U}$) < 1 (Andersen et al., 2009b). Because secondary phases and organic matter collect U derived from solution, they will show ($^{234}\text{U}/^{238}\text{U}$) > 1 and ($^{230}\text{Th}/^{238}\text{U}$) < 1 (Dequincey et al., 2002; Plater et al., 1992). Regolith is composed of residual primary minerals, secondary phases and organic matter, thus the U-series isotopic compositions of bulk regolith will integrate the composition of these components.

In theory, regolith production rates can be estimated by monitoring the U-series isotopic composition of residual primary minerals through a weathering profile. However, in the regolith, secondary phases and organic matter obscure the isotopic composition of residual primary minerals and introduce uncertainties; consequently, they can produce inaccurate regolith production rates. Until now, regolith production rates have been estimated analysing mostly untreated material (Dequincey et al., 2002; Dosseto et al.,
To address this issue, secondary phases and organic matter need to be removed from regolith without changing the isotopic composition of rock-derived minerals. A possible approach is to use sequential chemical extraction.

_Sequential extraction_ has been designed to remove trace metals associated with specific soil-fractions: exchangeable, carbonates, Fe- and Mn- oxides and organic matter (Schultz et al., 1998; Tessier et al., 1979). In the case of U-series isotopes, few authors have studied sequential extraction of soil (Blanco et al., 2004, 2005; Lee, 2009; Martin et al., 2015; Suresh et al., 2014). Martin et al. (2015) assessed the effectiveness of sequential extraction in removing secondary phases from a soil, marine and river sediments. They found that i) the removal of the secondary phases can be effectively monitored by measuring \( {^{234}U/^{238}U} \), ii) \( {^{234}U/^{238}U} \) decreases during sequential extraction as secondary phases are removed, and iii) additional mild HF/HCl etching further decreases \( {^{234}U/^{238}U} \) to a minimum, which indicates additional removal of secondary phases. However, these studies focused on top soil and sediments. In a weathering profile, bedrock, saprolite and soil are mineralogically different and the effectiveness of sequential extraction and etching in removing secondary phases may be different. Here we investigate if sequential extraction removes secondary phase from bedrock, saprolite and soil.

In this study, we monitored the U-series isotopic composition and U and Th concentrations of bedrock, saprolite and soil samples before and after sequential extraction, and during a 24-hr mild HF/HCl etching. We aimed at i) defining a pre-treatment method to isolate residual primary minerals from saprolite and ii) better understand the behaviour of the U-series isotopes during regolith development. We also constrained changes in mineralogy by analysing trends of variation of selected major elements during the treatment and by X-Ray Diffraction (XRD).

Our hypothesis is based on the studies by Lee (2009) and Martin et al. (2015). In a regolith sample, secondary phases and organic matter in regolith are expected to show \( {^{234}U/^{238}U} >1 \), while residual primary minerals should show an outer rind with \( {^{234}U/^{238}U} <1 \) and a core in secular equilibrium. Sequential extraction removes secondary phases and organic matter, and decreases the \( {^{234}U/^{238}U} \) activity ratio of the residue. However, sequential
extraction may not completely remove them. Because of this, etching is used to remove residual, secondary secondary phases and organic matter, and further decrease the \( \frac{^{234}U}{^{238}U} \) activity ratio to a minimum. The minimum \( \frac{^{234}U}{^{238}U} \) activity ratio represents the isotopic composition of residual primary minerals in the regolith. Further etching attacks the outer rind of the residual primary mineral, which is depleted in \(^{234}U\) relative to \(^{238}U\), and results in increasing the \( \frac{^{234}U}{^{238}U} \) activity ratio toward 1. We also hypothesise that sequential extraction does not change the U-series isotopic composition of residual primary minerals and bedrock. This is a key point, as we want to preserve the U-series isotopic composition of the residual primary minerals of the regolith to obtain accurate regolith production rates. Moreover, considering the U-series isotopes mobility, we expect residual primary minerals to decrease \( \frac{^{234}U}{^{238}U} \) and increase \( \frac{^{230}Th}{^{238}U} \) with decreasing regolith depth. This is because the extent of weathering increases with decreasing regolith depth and consequently isotopes fractionation increases.

2.3 Materials and methods

2.3.1 Environmental setting

The study area is located in Exeter, New South Wales, Australia (34°37’15.05” S 150° 19’08.30” E). The locality is at an elevation of 718 m and receives an annual average rainfall between 500 and 2000 mm. The underlying bedrock is a tertiary basalt and K-Ar dating measurements, carried on surrounding extrusions, have provided age estimates between 45 and 53 My (Wellman and McDougall, 1974). The soil is classified as Kraznozemic and consists of brown clays with high sesquioxide content and shows minor change in texture through the profile (Young, 1982). The Australian Soil Resource Information System classifies the land cover as grazing natural vegetation. Samples were collected from a flat-topped area in order to minimize input of colluvium due to lateral transport. A 2.7-meter-deep core was collected using a mechanical drilling system until the underlying bedrock was reached (see pictures in Appendix C). Two soils (S\text{UP} and S\text{LOW}), two saprolites (C\text{UP} and C\text{LOW}) and bedrock (BR) were collected respectively at 0.1, 0.9, 1.9, 2.5 and 2.7 m.
2.3.2 Analytical techniques

A thin section of the bedrock was prepared for optical analysis. The bedrock was ground, water washed using deionized water and dried in an oven at 60°C, before sequential extraction and etching. Soil and saprolite samples were dried in an oven at 60°C and an aliquot was analysed as untreated sample for U-series, major elements and Loss on Ignition (LOI) analysis. A second aliquot was homogenized with an agate mortar and wet sieved; the size fraction between 125 and 2000 μm was retained and underwent sequential extraction and etching. We retained the coarser fraction in order to facilitate the isolation of primary phases, which are generally more concentrated in this size fraction. The samples were prepared at Wollongong Isotope Geochronology Laboratory, University of Wollongong.

For sequential extraction, about 2 g of sample were placed in 50 ml perfluoralkoxy alkane (PFA) centrifuge tubes. Sequential extraction followed the procedure proposed by Tessier et al (1979), with one modification: the exchangeable fraction was removed using Mg(NO₃)₂ (Leleyter and Probst, 1999). All reagents were prepared with Millipore™ Milli-Q water (18.2 MΩ·cm at 25°C). Approximately 15 mg of sodium citrate per gram of sample were added to the sample at each step of sequential extraction to minimize U and Th re-adsorption (Lozano et al., 2011; Martin et al., 2015). After each step, the solid residue was separated from the solution by centrifugation at 3500 rpm for 10 minutes and the supernatant was removed using a Pasteur pipette. The sequential extraction procedure was performed using the following reagent solutions (with the grade and supplier in brackets): (i) exchangeable fraction was extracted using 8 ml of 1M Mg(NO₃)₂ (magnesium nitrate, Suprapur, Merck) per g of sample and agitated on an orbital shaker at room temperature for 50 minutes at 200 rpm. (ii) To extract carbonates the residue from step (i) was leached with 8 ml of 1M NaOAc (sodium acetate, Analytical grade, Merck) per gram of sample. The pH was adjusted to 5 using glacial HOAc (acetic acid, Reagent grade, ThermoFisher) and the solution was agitated on an orbital shaker for 5 hr at 200 rpm at room temperature. (iii) To eliminate Fe- and Mn- oxides, the residue from step (ii) was treated with 20 ml of 0.04M NH₂OH·HCl (hydroxylamine hydrochloride, TraceSELECT>99.9999%, Sigma-Aldrich) in 25% (v/v) HOAc at 95°C for 6 hr and agitated manually every 30 minutes. Finally, (iv) the organic matter was leached from the
residue of step (iii) with a three-stage leaching. Firstly, 3 ml of 0.02M HNO₃ and 5 ml of 30% H₂O₂ (Reagent grade, Merck) per gram of sample were added to the centrifuge tubes and pH was adjusted to 2 with concentrated HNO₃ 69% (ACS Reagent grade, Merck). The solution was kept at room temperature for 1 hr, and then the temperature was risen slowly to 85°C and left at the same temperature for 1.5 hr, agitating manually every 30 minutes. Secondly, 3 ml of 30% H₂O₂ per gram of sample were added and the pH was adjusted to 2 with concentrated HNO₃ 69%. The solution was heated at 85°C for 3 hr and agitated every 30 minutes. Finally, 5 ml of 3.2M NH₄OAc (ammonium acetate, TraceSELECT>99.9999%, Sigma-Aldrich) in 20% (v/v) HNO₃ per gram of sample were added and the total volume was taken up to 40 ml using Milli-Q water. The solution was agitated for 30 minutes on the orbital shaker at room temperature. At the end of the sequential extraction treatment an aliquot of about 100 mg was saved for U-series and major elements analysis. This aliquot is referred to as *leached* throughout the article.

The etching procedure was performed on the leached samples. 20 ml of 0.3M HF/0.1M HCl per gram of sample were added to the PFA centrifuge tube and agitated on the orbital shaker at 2000 rpm for 24 hr. An aliquot of about 100 mg of the solid residue was taken after 1, 2, 4, 8 and 24 hr. Each aliquot was transferred to a clean centrifuge tube and washed twice with 12 ml of Milli-Q water. Finally, all aliquots were dried in an oven at 70°C.

About 100 mg of each sample were spiked with ~30 mg of ²²⁹Th-²³⁶U tracer solution before acid dissolution. All reagents used during acid dissolution were Merck™ Suprapur grade. Samples were dissolved with 2.5 ml 32% HF and 0.5 ml 70% HClO₄ in 30 ml PFA vials at 100°C overnight. Dissolved sample solutions were dried to incipient dryness at 120°C. If dissolution was not fully completed, solutions were transferred to polytetrafluoroethylene (PTFE) digestion bombs and a mixture of 0.5 ml 69% HNO₃ and 1.5 ml concentrated 30% HCl was added. Bombs were heated at 200°C for more than 12 hr and then solutions were dried to incipient dryness at 120°C. The fully dissolved samples were then treated with 3 ml of 6M HCl. When necessary, H₃BO₃ was added to dissolve any residual fluorides. Resulting solutions were kept at 80°C overnight and dried to incipient dryness at 100°C. After that, 0.5 ml of 69% HNO₃ were added and then dried,
for 2 times. Finally, 2 ml of 1.5 M HNO₃ were added and the solutions were redissolved by 15 min sonication and heating at 100°C. The resulting solutions were then divided in two aliquots: a) a 0.1 ml aliquot was prepared for major element analysis; b) the remaining aliquot was loaded on chromatographic columns containing TRU resin (Eichrom) for the separation of U and Th, following Luo et al. (1997) method. The resulting solutions were dried to incipient dryness, and 0.5 ml of 31% H₂O₂ were added before drying down. A drop of 69% HNO₃ was added, dried down and finally the sample was dissolved in 2% HNO₃ before U-series isotopic analyses.

The U-series isotopic analyses were performed using Sims (2008) procedure on a ThermoFisher Neptune Plus Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometer at the Research School of Earth Science, Australian National University. Certified Reference Materials (CRM) U010 and synthetic standard OU Th’U’ were used for sample bracketing for U and Th analysis, respectively. Synthetic standards U005-A and UCSC Th’A’ were analysed as unknown solutions for U and Th, respectively and measurements were within 7‰ of the certified values (Richter et al., 2011; Rubin, 2001). Total procedure blanks were <53 pg for U and <214 pg for Th, while the average amounts of U and Th analysed in samples were 0.1 and 0.7 μg, respectively. Accuracy was assessed by analysing USGS QLO-1 rock standard and values were within error for U and Th concentrations (3.0% for U, 2.2% for Th), 0.4% for (²³⁴U/²³⁸U) and 6.5% for (²³⁰Th/²³⁸U), relative to certified values. The external analytical error was estimated by sample replicates.

Magnesium, Al, K, Ti, Fe and Zr concentration analyses were performed using an Agilent 7500 Series Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS) at University of Wollongong, Australia. The elemental concentrations were calculated by constructing a calibration curve using 12 standards, with concentration ranging from 0 to 500 ppb. The accuracy was determined analysing a gravimetric standard (QLO-1) and resulted < ±2.4%, < ±11.3%, < ±29.9%, ±6.5%, ±1.5% and ±4.8% for Mg, Al, K, Ti, Fe and Zr, respectively. The external analytical uncertainties were calculated as the relative standard error of sample replicates (see Tab. 2). The total procedure blank contributed on the
average sample content for less than 0.04%, 0.11%, 0.50%, 0.01%, 0.01%, 0.02% for Mg, Al, K, Ti, Fe and Zr respectively.

The XRD measurements were made on crushed samples. The samples were mounted on holders and analysed with a Phillips 1130/90 diffractometer set to 35 kV and 28.8 mA. A Spellman DF3 generator was set to 1 kW and samples were analysed using an automatic sample holder. The analysis were performed with 2-theta values between 4 and 70° at 2° per minute and a step size of 0.02. The data were then processed through GBC 122 control system, and Traces and SIROQUANT softwares. The accuracy obtained by XRD routine analysis is normally about ± 3% at the 95% confidence level (e.g. Hillier, 2000).

Loss on Ignition was determined at 550°C for 4 using the methodology recommended by Heiri et al. (2001).

### 2.4 Results and discussion

The XRD mineralogy data and major elements concentrations are presented in Table 2.1 and Table 2.2. We identified an immobile element and used it to estimate relative gains and losses of other elements.

#### 2.4.1 Ti as a conservative element

Titanium and zirconium are relatively immobile in regolith during weathering (Brimhall et al., 1992; Neaman et al., 2004; Pelt et al., 2008). Three observations suggest that Ti is immobile in our weathering profile. Firstly, untreated samples show increasing TiO₂ content with decreasing depth. Secondly, the linear relationship between Zr and TiO₂ concentrations (R^2=0.57; Figure 2.1) indicates that either they are not significantly fractionated during the experiment, or the two elements are mobilized at a similar rate, an unlikely possibility. Finally, the Zr/TiO₂ ratios in untreated bedrock, saprolite and soil remain relatively constant through the profile (RSD < ±20%). We chose Ti as the least mobile element because the Zr/TiO₂ ratios slightly decrease within sample during sequential extraction and etching.

Note that the concentration of Ti (and Zr) in all samples increase following sequential extraction but, in most cases, decrease after etching. This suggests that Ti is immobile.
during sequential extraction but may be mobilized by the etching protocol. Therefore, only in the case of etching, the immobility of Ti should be considered with more caution. The cause of Ti mobilization during etching remains unclear. Losses of elements relative to Ti observed during etching (e.g. decrease in U/TiO$_2$ ratios) may be underestimated, whereas gains may be artefacts.

![Figure 2.1. TiO$_2$ versus Zr concentrations for all samples of this study. The linear relationship showed has a R$^2$ = 0.57.](image)

### 2.4.2 Bedrock

A thin section of the untreated bedrock was prepared to define its mineralogy. Optical analysis showed that it is a fine-grained rock with larger microphenocrysts of olivine and plagioclase, cemented together by a fine glass matrix. The XRD data confirmed that the untreated bedrock is composed largely of olivine, pyroxene, plagioclase and K-feldspar,
and minor concentrations of magnetite and hornblende. While the $^{234}\text{U}/^{238}\text{U}$ activity ratio was in secular equilibrium, the $^{230}\text{Th}/^{238}\text{U}$ was lower than 1. This is surprising as the untreated bedrock is expected to be in secular equilibrium for both radioactive systems. It is possible that $^{230}\text{Th}$ is preferentially removed relative to $^{238}\text{U}$ during incipient dissolution. The preferential loss of Th over U during rock dissolution is supported by the experiments of Tilton et al. (1955) who observed that a greater fraction of labile Th relative to U was removed during a 5-minute acid stirring of ground rocks. The authors suggested that a large amount of mobile U and Th is present in mineral fractures and interstices and are therefore easily mobilizable during incipient rock dissolution.

Following sequential extraction, we observed a loss of Mg, K, Fe and Al relative to Ti (Figure 2.2), while the XRD data indicated loss of olivine. Olivine dissolution explains the losses of Mg and Fe, while other labile phases in basaltic rocks are glass and inter-granular phases (Chesworth et al., 1981; Chesworth et al., 2004; Eggleton et al., 1987; Tieh et al., 1980). Glass commonly concentrates K and Al (e.g. Karrat et al., 1998) and can explain the loss of these elements from the bedrock. However, XRD cannot detect glass and inter-granular phases as their structure is amorphous. Despite sequential extraction having been designed to remove secondary phases and organic matter (Tessier et al., 1979), some of the steps are performed at low pH and temperatures up to 96°C for several hours, which could be conditions aggressive enough to dissolve glass and olivine. For instance, glass dissolution experiments have been performed at pH 3 (e.g. Möller and Giese, 1997; Oelkers and Gislason, 2001). Similarly, studies have carried out dissolution experiments of olivine at temperatures between 25 and 65 °C, and pH between 2 and 5 (Chen and Brantley, 2000; Valsami-Jones et al., 1998). In natural environments, Chesworth et al. (1981) observed results similar to our laboratory experiments. They studied the evolution of the elemental composition of a basaltic profile and suggested rapid dissolution of glass and olivine from the unweathered rock, associated with losses of Mg, Na and K during early stages of weathering. The authors concluded that when labile phases are completely dissolved, the release of Mg and K reduces, indicating the presence of residual, more resistant minerals such as plagioclases and pyroxenes.
Following sequential extraction, we observe a loss of U and Th (Figure 2.3) probably due to the dissolution of glass and inter-granular phases. Sequential extraction resulted in the removal of ~72% and ~64% of U and Th relative to Ti from the bedrock. These losses suggest dissolution of one or several labile, U- and Th-bearing phases. As discussed above, the phases most likely dissolved during sequential extraction are olivine and glass, but large amount of U and Th could also be retained in unstable inter-granular phases (Tieh et al., 1980). Olivine usually contains very low U and Th (Harmon and Rosholt, 1982), in contrast with glass (Dostal and Capedri, 1975; Dostal et al., 1976). Glass concentrates U and Th because of their incompatibility during magma differentiation (Hofmann, 1988). If we consider a bedrock with 1 ppm of U and 22 wt.% of olivine, and assuming a U concentration in olivine of 0.01 ppm (Harmon and Rosholt, 1982), the olivine would contribute only ~0.22% of the total U present in the bedrock. This suggests...
that olivine is unlikely to be responsible for the observed loss of U following sequential extraction. In contrast, glass contents in basalt are commonly of the order of 10 wt.% (Robertson and Peck, 1974), and reported U concentrations in glass are between 0.2 and 11 ppm (Aumento, 1971; Walton et al., 1981). Assuming glass concentration in our basalt of 10 wt.%, containing 2 ppm of U, the glass would contribute 20% of the total U budget in the bedrock. The remaining fraction of U lost may be supplied by inter-granular phases. Uranium in inter-granular phases could be released due to the experimental conditions applied during sequential extraction. For instance, Tilton et al. (1955) found that 34 and 42% of U and Th were removed from inter-granular phases of a granitic bedrock by a 5-minutes stirring with 6 M HCl. This suggests that the dissolution of inter-granular phases can result in the large losses of U and Th.

Figure 2.3. U and Th to TiO$_2$ ratios for the untreated, leached and etched bedrock. Error bars represent propagated external relative analytical uncertainties (RSE) reported in Tab. 3. When error bars are not shown, they lie within symbol size.
After sequential extraction, the $^{234}\text{U}/^{238}\text{U}$ activity ratio increased by ~1% and $^{230}\text{Th}/^{238}\text{U}$ by ~40% (Figure 2.4). The lack of significant variation in the $^{234}\text{U}/^{238}\text{U}$ ratio suggests that sequential extraction removes phases with isotopic composition similar to the bedrock. In contrast, the increase in $^{230}\text{Th}/^{238}\text{U}$ is explained by the preferential loss of U over Th during glass dissolution and the removal of inter-granular U and Th. Thus, it is not recommended to perform sequential extraction on bedrock because primary phases can be lost and artefacts in $^{230}\text{Th}/^{238}\text{U}$ introduced.

Figure 2.4. $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ for the untreated, leached and etched bedrock. Error bars represent external relative analytical uncertainties (RSE) reported in Tab. 3. When error bars are not shown, they lie within symbol size.

The XRD data suggested loss of olivine and, possibly, plagioclases during etching, while the rest of the primary minerals remained unchanged (Table 2.1). We observed a loss of K and Al relative to Ti during the first hour of etching, while for longer duration their abundances remained relatively constant (Figure 2.2). In contrast, Mg and Fe concentrations showed a slight, but continuous decrease relative to Ti during the 24 hr of
etching. Whereas the continuous losses of Mg and Fe confirm olivine dissolution during the 24 hr etching, K and Al suggest that glass is dissolved only during the first hour. After 1 hr of etching, it is possible that glass is no longer present in the residue or our methodology is not able to detect further losses. Thorium and uranium concentrations relative to Ti did not significantly change; however, because Ti concentrations decrease after the first hour of etching, it is possible that losses of U and Th, as well as other elements, are underestimated. This suggests that etching removes phases containing U and Th, confirming dissolution of glass and possibly plagioclase (in addition to olivine).

During etching the $^{(234)U/238U}$ and $^{(230)Th/238U}$ activity ratios increased continuously relatively to the leached bedrock, showing values greater than one. This is unexpected, because during mineral dissolution $^{234}U$ is thought to be more mobile than $^{238}U$ and weathering products are expected to show $^{(234)U/238U} < 1$ (e.g. Chabaux et al., 2003; Dequincey et al., 2002; Dosseto et al., 2008a; Ma et al., 2010). Therefore, the increase in $^{(234)U/238U}$ indicates that phases depleted in $^{234}U$ relative to $^{238}U$ are removed. Several authors have reported the removal of phases depleted in $^{234}U$ relative to $^{238}U$ during acid-leaching experiments (Essien, 1990; Romer and Rocholl, 2004; Sheng and Kuroda, 1986b; Shirvington, 1983). For instance, Sheng and Kuroda (1986a) performed acid leaching experiments on carnotite and observed $^{(234)U/238U} > 1$ in the residue. They suggested that $^{234}U$ is recoiled from a labile, U-rich phase to an adjacent resistant, U-poor phase (Sheng-Kuroda effect). As a result, the resistant, U-poor phase becomes enriched in $^{234}U$ with respect to $^{238}U$, while the labile, U-poor phase becomes depleted in the same isotope. During dissolution, if the U-rich phase is preferentially removed, the residue will be enriched in $^{234}U$ relative to $^{238}U$. This mechanism is mainly influenced by two factors. First, the larger the difference in U contents between the two adjacent phases, the more effective the transfer of the radiogenic nuclides is (Sheng, 1986; Sheng and Kuroda, 1986a). Second, the size of the U-poor mineral relative to the $^{234}$Th $\alpha$-recoil range, that is 55 nm (Kigoshi, 1971), must be small enough to produce a measurable isotopic fractionation. Recently Tanaka et al. (2015) performed a one-step acid leaching on powdered basaltic rocks, and obtained results similar to ours. The authors concluded that the $^{(234)U/238U}$ and $^{(230)Th/238U}$ above unity observed in the acid-leaching residue was the result of alpha-recoil of $^{234}U$ and $^{230}Th$ from labile to resistant phases in the groundmass.
In our study the labile U-rich phase is most likely glass, while resistant U-poor phases are fine-grained feldspars and pyroxene present in the groundmass. Therefore, we suggest that in the bedrock, $^{234}\text{U}$ is recoiled from the glass into fine-grained feldspars and/or pyroxenes, resulting in glass with $(^{234}\text{U}/^{238}\text{U}) < 1$, and feldspar and pyroxene with $(^{234}\text{U}/^{238}\text{U}) > 1$. The increasing $(^{230}\text{Th}/^{238}\text{U})$ during etching can be explained in two ways. First, etching removes more U than Th because of their different mobility. Alternatively, the $^{234}\text{U}$ recoiled into feldspars and/or pyroxene has enough time to equilibrate with its daughter $^{230}\text{Th}$ (of the order of 300 kyr). The equilibration would result in feldspars and/or pyroxene with $(^{230}\text{Th}/^{238}\text{U}) > 1$ and glass with $(^{230}\text{Th}/^{238}\text{U}) < 1$. As etching removes glass, its residue will show increasing $(^{230}\text{Th}/^{238}\text{U})$. For etching duration >1 hr, we observed a continuous increase in $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ values, in correspondence with plagioclase and olivine dissolution. It is also possible that our methodology is not able to detect small variations in glass content that occur after 1 hr of etching. In addition, a minor, U-rich phase could be dissolved, for which we have no geochemical data (e.g. phosphorus for apatite) and could be below XRD detection limit. Indeed, relative to the 1 hr etched sample, a U loss of only 5% is required to account for the observed increase in $(^{234}\text{U}/^{238}\text{U})$.

It is important to note that nuclides recoiled into pyroxenes and/or feldspars should be easily mobilised during sequential extraction, since loosely embedded in recoil tracks (Fleischer, 1980). The observed $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ greater than 1 suggests that annealing of these phases occurs, thus preventing loss of the nuclides in absence of significant pyroxene and feldspar dissolution (Eyal and Fleischer, 1985; Tanaka et al., 2015).

### 2.4.3 Saprolite

By comparing untreated bedrock and saprolite we aimed at investigating the effects of the conversion of bedrock into saprolite on the mineralogy, the major element and the U-series isotopic composition of the regolith. The XRD data showed that the untreated saprolite had a lower olivine, plagioclase, K-feldspar and pyroxene content, compared to the untreated bedrock, while a significant abundance of clay minerals was present (Table 2.1).
The MgO/TiO₂ and K₂O/TiO₂ ratios were lower in the saprolite compared to the bedrock, indicating a loss of these elements during the conversion of the bedrock into saprolite. In contrast, Al₂O₃/TiO₂, Fe₂O₃/TiO₂, U/TiO₂ and Th/TiO₂ ratios and the \(\frac{^{234}\text{U}}{^{238}\text{U}}\) and \(\frac{^{230}\text{Th}}{^{238}\text{U}}\) activity ratios remained almost unchanged (Figures 2.5 and 2.6). The loss of Mg and K is explained by the weathering of olivine and K-feldspar. Because olivine and glass have the same susceptibility to weathering, it is likely that glass is also dissolved (Eggleton et al., 1987). As we observe a loss of Al- and Fe-bearing minerals (feldspars, pyroxenes and olivine), the constant Al₂O₃/TiO₂ and Fe₂O₃/TiO₂ is explained by the in-situ conversion of these phases into secondary phases, i.e. clays. In principle, weathering of silicate minerals is mostly driven by hydrolysis reactions (Trescases et al., 1992), in which cations located in the mineral lattice are replaced by hydrogen ions from solution. During these processes less mobile elements, such as Mg and K, are removed, while less mobile elements, such as Al and Fe, remain and recombine to form clays (Arslan et al., 2006). For instance, weathering of olivine initially results in the formation of Fe-oxides and hydrated Mg-silicate. Successively, Mg is lost while Fe remains; the latter recombines with SiO₄ tetrahedra to form, depending on the weathering conditions, smectite, montmorillonite, hematite and/or goethite (Delvigne et al., 1979). Similarly, feldspar commonly weather to kaolinite, secondary mica (e.g. sericite) and/or allophane (Ollier and Pain, 1996) and glass into Fe-rich kaolinite (Arslan et al., 2006).
Figure 2.5. U, Th, MgO, Al₂O₃, K₂O and Fe₂O₃ to TiO₂ ratios versus depth for untreated samples. Error bars represent propagated external relative analytical uncertainties (RSE) reported in Tab. 2. When error bars are not shown, they lie within symbol size.

The constant U/TiO₂ and Th/TiO₂ ratios between the untreated bedrock and saprolite imply that there is no loss of U and Th during clay formation. Similarly, the (²³⁴U/²³⁸U) and (²³⁰Th/²³⁸U) activity ratios showed similar values, confirming that these nuclides are not considerably lost during clay formation. Note that the estimation of regolith production rates is based on the fractionation among the U-series isotopes. Therefore, because U and Th are not fractionated during the conversion of primary minerals into clays, the latter phases need to be preserved.
The untreated saprolite was sieved at 125 μm and the coarser fraction was retained. The fraction coarser than 125 μm displayed MgO/TiO₂ and Fe₂O₃/TiO₂ ratios similar to those of the untreated saprolite, but higher K₂O/TiO₂ and Al₂O₃/TiO₂ ratios (Figure 2.7). The gain in K and Al may suggest that the coarser size fraction is enriched in K-feldspars. Sieving had little effect on the U and Th concentrations and activity ratios. This suggests that U and Th isotopes are uniformly distributed across these size fractions. The higher U/TiO₂ value in the coarse fraction of the lower saprolite may be an analytical artefact (Figure 2.8); the U concentration is anomalously high compared to all other samples, while TiO₂ concentration is similar. The grain-size fraction coarser than 125 μm was used for sequential extraction and etching, as described in the method section.
The XRD data did not show any loss of primary minerals but indicated removal of clays: ~30 and ~12% in the lower and upper saprolite, respectively. Note that the decrease in clays is likely to represent the combined effect of sequential extraction and sieving. It was not possible to differentiate between the two, considering that we were unable to undertake XRD analysis on sieved samples. Following sequential extraction of the saprolite, Mg, K, Al, U, and to a lesser extent Th were lost (Figure 2.7). This is likely to be explained by the loss of clays and possibly other phases such as Fe-oxides, during this treatment.
Sequential extraction had opposing effects on the $^{234}\text{U}/^{238}\text{U}$ activity ratios of the saprolite (Figure 2.9). In the lower saprolite, it resulted in a decrease in the $^{234}\text{U}/^{238}\text{U}$ activity ratio to a value below 1. For instance, loss of Al following sequential extraction suggests clays dissolution, as Al is a major component of most clay minerals. Indeed, hydroxylamine, which is used during sequential extraction, is known to dissolve Al-bearing clays (e.g. Ross et al., 1985). This indicates the removal of phases with $^{234}\text{U}/^{238}\text{U}$ >1, possibly clays as suggested by XRD and major element data. Above we saw that untreated bedrock and saprolite showed similar $^{234}\text{U}/^{238}\text{U}$. This was explained as a lack of loss or gain of nuclides during clay formation, possibly implying that clays have a $^{234}\text{U}/^{238}\text{U} = 1$. If this was the case, we should not observe a change in $^{234}\text{U}/^{238}\text{U}$ following the loss of clays during sequential extraction. To explain this discrepancy, it is possible that clays have variable $^{234}\text{U}/^{238}\text{U}$ depending on which primary minerals they
are derived from. In the previous section, we saw that pyroxenes and feldspars could be enriched in \(^{234}\text{U}\) relative to \(^{238}\text{U}\) as a result of Sheng-Kuroda effect. If the transformation of these minerals into clays occurred without loss or gain of nuclides, this would result in clays with \((^{234}\text{U}/^{238}\text{U}) > 1\). Thus, the loss of these clays during sequential extraction would account for the observed \((^{234}\text{U}/^{238}\text{U}) < 1\) in the residue.

Figure 2.9. \((^{230}\text{Th}/^{238}\text{U})\) and \((^{234}\text{U}/^{238}\text{U})\) for the untreated, leached and etched upper and lower saprolite. Error bars represent propagated external relative analytical uncertainties (RSE) reported in Tab. 3. When error bars are not shown, they lie within symbol size.

In the upper saprolite, sequential extraction resulted in an increase in \((^{234}\text{U}/^{238}\text{U})\) to values greater than 1. This could be explained by the loss of clays with \((^{234}\text{U}/^{238}\text{U}) < 1\). The decrease in Al/Ti ratio supports the hypothesis of clay dissolution occurring during sequential extraction (Figure 2.7). In the previous section, we proposed that glass could be characterised by a \((^{234}\text{U}/^{238}\text{U}) < 1\) as a result of the Sheng-Kuroda effect. Hence, clays produced by alteration of glass could inherit the \(4/8 < 1\). Their loss during sequential extraction of the upper saprolite could explained the observed \(4/8 > 1\) in the residue.
Sequential extraction resulted in an increase of the \(^{(230\text{Th}/238\text{U})}\) activity ratios in both saprolites (Figure 2.9). This suggests a preferential loss of U over Th during the removal of clays and possible other secondary phases. This also indicates residual primary phases present in the saprolite are characterised by a \((^{230}\text{Th}/^{238}\text{U}) > 1\). This is supported by results from the bedrock experiment, which showed that residual primary minerals at the end of sequential extraction and etching have a \((^{230}\text{Th}/^{238}\text{U}) > 1\). Therefore, it is possible that sequential extraction of saprolite exposes their isotopic composition.

The aim of etching is to remove labile phases left after sequential extraction. X-ray Diffraction data did not suggest systematic variation in mineralogy during etching. In both saprolites, there was no change in Fe\(_2\)O\(_3\)/TiO\(_2\) and K\(_2\)O/TiO\(_2\). In the lower saprolite, Al\(_2\)O\(_3\)/TiO\(_2\) and MgO/TiO\(_2\) ratios both increased and decreased during treatment. In the upper saprolite, these two elements were continuously lost. This could be the result of minor loss of primary minerals, undetected by XRD, and/or of Al- and Mg-bearing poorly-crystalline phases (e.g. clays). While Th concentrations remained unchanged for both saprolites, U was removed during the first hour of etching. Note that high U/TiO\(_2\) and Th/TiO\(_2\) ratios in the upper saprolite after 1 hr of etching are possibly due to anomalously low TiO\(_2\) concentrations. The \((^{234}\text{U}/^{238}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\) activity ratios increased during the first hour of etching to values above 1, and remained relatively constant for longer durations. These results indicate that etching removes phases containing Al, Mg and U, and with \((^{234}\text{U}/^{238}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\) < 1. This can be explained by nearly complete removal of secondary phases after 1 hr of etching. This would produce a residue composed by resistant primary minerals enriched in \(^{234}\text{U}\) relative to \(^{238}\text{U}\), such as pyroxenes and feldspars. This hypothesis is supported by two observations: i) etching produces a residue with \((^{234}\text{U}/^{238}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\) similar to the resistant primary minerals found in the bedrock after sequential extraction and etching (see Figure 2.4); and ii) the increase in \((^{234}\text{U}/^{238}\text{U})\) occurs during the first hour of etching; this suggests the nearly complete removal of labile phases (e.g. clays).

In summary, sequential extraction followed by 1 hr of etching removes secondary phases such as clays and exposes the U-series isotopic composition of residual primary minerals.
As during the conversion of bedrock-forming primary minerals to clays the U-series are not fractionated, sequential extraction and etching are not needed.

2.4.4 Soil

When compared to the untreated material, the soil had lower olivine, pyroxene, plagioclase and clay contents than the saprolite (Table 2.1). Surprisingly, quartz was detected suggesting aeolian deposition is an important component of the soil mineral budget. This could also account for the lower abundance of other minerals.

Relative to Ti, there was a loss of Mg, gain of K and, similarly to what we observed in the untreated bedrock and saprolite, Fe and Al remained nearly unchanged (Figure 2.5). The loss of Mg could be explained by the dissolution of Mg-bearing phases such as olivine and clays. The gain in K could be accounted for by the aeolian deposition of K-rich phases along with quartz.

In contrast, untreated soil gained U and Th relative to Ti when compared to the untreated saprolite (Figure 2.5). The soil showed \( {^{234}U}/^{238}U \) >1 and \( {^{230}Th}/^{238}U \) <1 (Figure 2.6). The U-series activity ratios suggest that soil gains U and Th (Andersen et al., 2013; Ma et al., 2010). This can be explained in two ways. First, the U and Th gained by the soil could be retained in organic matter; the LOI data (Table 2.2) support this in the upper soil, in which they suggest greater concentration of organic matter relative to the saprolite. In contrast, the concentration of organic matter in the lower soil is the same as the saprolite and it does not explain the addition of U and Th. Second, it is possible that secondary phases containing U, Th and K, but with low Al and Fe content, are precipitated or adsorbed into the soil from soil pore water. In both cases, organic matter and secondary phases are expected to show \( {^{234}U}/^{238}U \) >1 and \( {^{230}Th}/^{238}U \) <1 (Dequincey et al., 2002; Plater et al., 1992) and would explain the soil isotopic composition of the soil. These phases obscure the isotopic composition of primary minerals.

The removal of the grain size fraction <125 \( \mu m \) resulted in an increase in K and Al contents relative to Ti, while Fe and Mg remained nearly unchanged (Figure 2.10). This shows that the grain size fraction < 125 \( \mu m \) is depleted in Al and K. The U concentrations and the U-series activity ratios did not significantly change after sieving (Figures 2.11
This suggests homogeneous U-series isotopic composition across size fraction. For sequential extraction and etching, we retained the size fraction coarser than 125 μm.

Figure 2.10. Mg, K, Fe and Al oxides to TiO₂ ratios for untreated, sieved, leached and etched soil. Close symbols represent the lower soil, while the open symbols the upper soil. Error bars represent propagated external relative analytical uncertainties (RSE) reported in Tab. 2. When error bars are not shown, they lie within symbol size.

After sequential extraction, there was no significant change in mineral abundances compared to the untreated soil (Table 2.1). However, we observed losses of Mg, K, Al, U and Th relative to Ti, while Fe remained unchanged (Figures 2.10 and 2.11). Sequential extraction resulted in a decrease in (²³⁴U/²³⁸U) from values greater to lower than 1, while the opposite was observed for (²³⁰Th/²³⁸U) (Figure 2.12). These results suggest that sequential extraction removes phases containing Mg, K, Al, U and Th, with (²³⁴U/²³⁸U) >1 and (²³⁰Th/²³⁸U) <1. Possibly, secondary phases, such as clays, and organic matter precipitated from the solution, which are expected to be characterised by (²³⁴U/²³⁸U) >1 and (²³⁰Th/²³⁸U) <1, are removed. These phases obscure the U-series isotopic composition of the residual primary minerals and are not needed to estimate regolith production rates.
Figure 2.11. U and Th to TiO\textsubscript{2} ratios for the untreated, leached and etched upper and lower soil. Error bars represent propagated external relative analytical uncertainties (RSE) reported in Tab. 3. When error bars are not shown, they lie within symbol size.
During the 24 hr of etching, we observed small increase in pyroxene and plagioclase contents, associated with a small decrease in K-feldspar, while quartz and clays increased and decreased. Aluminium abundance varied slightly, while Mg, K and Fe remained substantially unchanged, relative to Ti (Figure 2.10). The Fe₂O₃ concentrations for the upper soil (S_up) after 1 hr etching and at the end of etching are anomalously high (Table 2.2); this could be the result of contamination and these two data points have not been plotted in Figure 2.10. Titanium-normalised U and Th contents show little variations during etching (Figure 2.11). Similarly, the (²³⁴U/²³⁸U) and (²³⁰Th/²³⁸U) activity ratios remained mostly unchanged, suggesting that etching does not remove phases containing U and Th (Figure 2.12). Element content normalized to Ti and XRD data do not indicate mineral losses; it seems that etching has little effect on soil that has undergone sequential extraction. However, a closer look at the element concentrations shows loss of Ti, Fe and

Figure 2.12. (²³⁰Th/²³⁸U) and (²³⁴U/²³⁸U) for the untreated, leached and etched upper and lower soil. Error bars represent propagated external relative analytical uncertainties (RSE) reported in Tab. 3. When error bars are not shown, they lie within symbol size.
Zr following 1 hr of etching. This suggests that one or more phases containing these elements are removed, undetected by XRD. Note that mobilization of Ti during the first hour of etching explains the increase in U/Ti and Th/Ti, indicating that, in this specific case, Ti is mobilized whereas U and Th are not. Hence, the gain of U and Th shown in Figure 2.12 after 1 hr of etching may be an artefact. This is confirmed by the fact that the dissolution of Fe-Zr-Ti-bearing phases does not affect the U-series isotopic composition of soil samples. It is also important to note that the presence of allochthonous quartz is unlikely to significantly affect the U-series isotopic composition of the soil residue, because of its low content of U and Th.

2.4.5 Implications

During the conversion of the bedrock into the saprolite, U-series isotopes are not fractionated and remain in newly formed clays. Because sequential extraction removes clays, at least partially, it is not recommended to apply this treatment to saprolite samples.

In the untreated soil, we found that sequential extraction efficiently removes secondary phases and organic matter. In addition, mild HF/HCl etching resulted in no improvement. This is in contrast with Martin et al. (2015), who found that etching was necessary to completely remove secondary phases and organic matter. In any case, we obtained the same isotopic composition either etching is applied or not.

To estimate regolith production rates using the U-series isotopes only secondary phases that are not ultimately originated from the bedrock and organic matter need to be removed. In our study, we recommend analysing untreated saprolite and sequentially extracted soil. The resulting evolution of the $^{234}$U/$^{238}$U activity ratios through the profile (Figure 2.13) slightly increase between the bedrock and the saprolite, and then decrease below 1 in the soil. The $^{230}$Th/$^{238}$U activity ratios remain unchanged between the bedrock and the saprolite and then increases in the soil. This suggests that weathering processes that operate during the transformation of the bedrock into the saprolite are slow and/or result in no significant loss or gain of U-series isotopes, as they create small variations in isotopic composition. Isotopic fractionation may still occur, but all the nuclides remain in the bulk saprolite and are not mobilized. In contrast, during the transition between saprolite and soil, weathering processes are more intense and create isotopic fractionation.
One could argue that different treatments would introduce artefacts in the estimates the U-series isotopic composition of the regolith profile. However, this study points out that saprolites and soils contain secondary phases of different origin and organic matter that need to be treated in the different ways. While secondary phases originated from the bedrock and that have not fractionated U and Th need to be preserved, organic matter and other secondary phases need to be removed to expose the isotopic composition of primary minerals.

### 2.5 Conclusions

We applied sequential extraction and mild HF/HCl etching to a bedrock, two saprolites and two soils of a basaltic weathering profile. The aim was to define a pre-treatment method to isolate primary minerals from the regolith.
This study provides insights on the behaviour of U-series during regolith development. The untreated bedrock was in secular equilibrium for $^{234}\text{U}/^{238}\text{U}$ but not for $^{230}\text{Th}/^{238}\text{U}$, indicating fractionation between $^{238}\text{U}$ and $^{230}\text{Th}$. The untreated saprolite showed activity ratios similar to the bedrock; we inferred that during the conversion of the bedrock into the saprolite olivine, feldspar, pyroxene and glass are converted into clays. During this process, the U-series isotopes fractionate within the material (i.e. ejection of nuclides from glass and implantation into pyroxene) but overall they are not significantly gained or lost. Because the data suggest that sequential extraction removes variable extent of clays in the saprolite, it is not recommended to perform it on saprolite samples. The soil showed $^{234}\text{U}/^{238}\text{U}>1$ and $^{230}\text{Th}/^{238}\text{U}<1$; we inferred the presence of secondary phases and organic matter that obscure the isotopic composition of residual primary minerals. These phases need to be removed, as they introduce uncertainties in the model to estimate regolith production rates. Our study suggests that sequential extraction efficiently removes secondary phases and organic matter. In contrast, mild HF/HCl etching does not produce significant effect on the soil.

To isolate from the regolith the phases containing U-series isotopes originated from the bedrock we suggest to i) use the untreated bedrock and untreated saprolite, and ii) apply sequential extraction to soil to isolate primary minerals (Figure 2.13). This is expected to significantly improve the accuracy of regolith production rates estimated using U-series isotopes. The bedrock should not be treated, as no phases need to be removed from it; in this study, we only tested bedrock response to sequential extraction and etching. The saprolite contains clays derived from the weathering of primary minerals. Because during the transformation of the bedrock into saprolite the U-series isotopes are not added or fractionated, the clays need to remain in the sample. In contrast, the soil contains secondary phases not derived from the bedrock and organic matter; these phases need to be removed to expose the U-series isotopic composition- of residual primary minerals. In this study, we found that secondary phases and organic matter contained the soil can be removed by sequential extraction.

This study provides a promising, simple and cost-effective pre-treatment method to enhance the accuracy of regolith production rates estimated using U-series isotopes. It
also emphasizes the importance of carefully evaluate the different effect of treatments, such as sequential extraction, on regolith, saprolite and soil. Moreover, this article does not provide a single pre-treatment method suitable to isolate residual primary minerals in all regolith profiles. It shows that the U-series isotopes can be used to monitor the completeness of it and to adjust the pre-treatment steps to obtain the desired result in the different areas of the regolith.

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### Table 2.1. Mineralogical abundances (in wt.%) determined by XRD.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Olivine</th>
<th>Pyroxene</th>
<th>Plagioclase</th>
<th>K-feldspar</th>
<th>Quartz</th>
<th>Clays</th>
<th>Hematite</th>
<th>Others</th>
<th>TOTAL</th>
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</thead>
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<tr>
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<td>22</td>
<td>16</td>
<td>47</td>
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<td>4</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>15</td>
<td>55</td>
<td>12</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>BR 24h etching</td>
<td>6</td>
<td>20</td>
<td>51</td>
<td>16</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
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</tr>
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<td>14</td>
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<td>1</td>
<td>58</td>
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The accuracy obtained by XRD routine analysis is normally about ± 3% at the 95% confidence level (e.g. Hillier, 2000). “Others” include zircon, xenotime, mica, allanite, epidote and hornblende, and are present in concentrations < 5 wt.%. 

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Tables
Table 2.2 Concentration of selected elements in wt.% and ppm. Errors are internal analytical uncertainties (RSD). The estimated external relative analytical uncertainties (SE) were calculated from replicate analysis of rock standards and samples. Loss on Ignition (LOI) was measured at 500°C.

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<th>Sample name</th>
<th>MgO (wt.%)</th>
<th>RSD</th>
<th>Al₂O₃ (wt.%)</th>
<th>RSD</th>
<th>K₂O</th>
<th>RSD</th>
<th>TiO₂ (wt.%)</th>
<th>RSD</th>
<th>Fe₂O₃</th>
<th>RSD</th>
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<th>RSD</th>
<th>LOI (wt.%)</th>
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QLO-1

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<th>K₂O</th>
<th>RSD</th>
<th>TiO₂ (wt.%)</th>
<th>RSD</th>
<th>Fe₂O₃T (wt.%)</th>
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<th>Zr (ppm)</th>
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Estimated external relative analytical uncertainties (RSE): ±4.9% ±0.15% ±3.18% ±12.9% ±6.4% ±9.6%
Table 2.3. U-series results. Errors are internal analytical uncertainties (2SE). The estimated external relative analytical uncertainties (RSE) were calculated from replicate analysis of rock standards and samples; the highest error is reported in this table and used as uncertainties for the error bars in next figures.

<table>
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<th>U (ppm)</th>
<th>2SE</th>
<th>Th (ppm)</th>
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<th>($^{230}$U/$^{238}$U)</th>
<th>2SE</th>
<th>($^{230}$Th/$^{238}$U)</th>
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<td>±0.2%</td>
<td>±4.8%</td>
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References


Sequential extraction and mineral separation to assess U-series isotopes fractionation during granitic pedogenesis

Davide Menozzi¹,* , Anthony Dosseto¹ and Leslie P.J. Kinsley²

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Telephone: (+61) 0478 761 253
3.1 Abstract

The assessment of soil sustainability is important to insure the future of our societies, as soil provides food and ecosystem services. Recently, the uranium-series (U-series) isotopic composition of weathering profiles has been used as a geochemical tool to assess regolith production rates, which can give information to assess soil sustainability. Most of the published rates have been estimated on bulk regolith. However, the presence in the sample of phases not derived from the bedrock (e.g. solution-derived phases and organic matter) has been identified as a possible issue that decreases the accuracy of this technique.

Here we assess whether minerals separated form a regolith profile (quartz and biotite) and/or regolith that underwent sequential extraction – a chemical procedure designed to remove secondary phases and organic matter from soil – record U-series isotopes fractionation of phases derived from the bedrock, without the influence of solution-derived phases and organic matter. The isotopic analyses are integrated with mineralogical and major elements analyses to understand processes occurring during pedogenesis. Sequential extraction and/or mineral separation may be used as pre-treatment for U-series isotopes analyses to improve the accuracy of regolith production rates.

The bulk samples indicate that during the conversion of the bedrock into saprolite a pool of U and Th is mobilized, mostly from the dissolution of labile phases (biotite and feldspars), whereas in soil, U and Th adsorption is observed. Sequential extraction does not remove major mineral phases from the samples. However, pools of U and Th are mobilized, whether in the bedrock or in the regolith. These pools may have been adsorbed from pore water onto regolith components during pedogenesis and/or result from the dissolution of phases on grain boundaries and/or inclusions. We do not recommend sequential extraction for this type of weathering profiles as phases derived from the bedrock may be removed. Quartz separates show a general loss of U throughout the profile, while Th is gained in the saprolite and lost in the soil. The isotopic analyses also suggest U-series nuclide adsorption onto quartz in the soil. Quartz revealed to be a suitable mineral to study U-series nuclides fractionation during
pedogenesis; however, a treatment to remove nuclides adsorbed on its surface is needed. Biotite acts as a “sponge” for U-series nuclides and is not suitable for U-series isotope analyses. In summary, mineral separation can contribute to better understand U-series nuclide fractionation during pedogenesis.

3.2 Introduction

Soil is a fundamental resource for societies and the environment; for instance soil provides food, ecosystem services (Clothier et al., 2011) and contributes to biodiversity (Brussaard, 1997). Its sustainability is an important issue and the balance between the rate of soil erosion and production controls it. While rates of erosion are well understood and have been increasing due to modern land use (Pimentel et al., 1995), rates of soil production are still not well known. Therefore, it is important to investigate rates and mechanisms of soil formation to assess its sustainability.

The uranium-series (U-series) isotopic composition of the regolith – namely saprolite and soil – can be used to study processes at work in the weathering profile (Hansen and Stout, 1968; Rosholt et al., 1966). In a bedrock that has remained unweathered for more than 1 Myr, U-series isotopes will be in secular equilibrium; i.e. all nuclides will have the same activity and daughter-parent activity ratios will equal one (Bourdon et al., 2003). The mobility of U during weathering processes greatly depends on its oxidation state. In reducing conditions, U is in the +4 oxidation state, which is relatively immobile, while in oxidising environments such as during Earth surface processes, it is in the more mobile +6 state. In contrast, Th has only one oxidation state (+4) and is considered immobile, although organic ligands significantly increase its mobility (Chabaux et al., 2003). During water-rock/regolith interaction, the isotopes of U and Th fractionate and produce radioactive disequilibrium in the residue (i.e. nuclides have different activities). This commonly results in weathering products (soil and saprolite) showing \( \frac{230}{238} \text{Th}/\frac{234}{238} \text{U} > 1 \) – where parenthesis denote activity ratios through this article (Chabaux et al., 2003; Dosseto et al., 2008b). In addition, during
weathering processes the mobility of $^{234}\text{U}$ is greater than $^{238}\text{U}$. This is due to i) direct ejection of $^{234}\text{U}$ from the outer rind of minerals following alpha-decay of $^{238}\text{U}$ (Kigoshi, 1971), and ii) preferential leaching of alpha-recoiled atoms (i.e. $^{234}\text{U}$) which are located in damaged sites of the mineral lattice as a result of radioactive decay (Chabaux et al., 2008). Consequently, the residue of water-rock/regolith interaction and the aqueous solution are expected to show $(^{234}\text{U}/^{238}\text{U}) < 1$ and $(^{234}\text{U}/^{238}\text{U}) > 1$ (Andersen et al., 2009b; Dosseto et al., 2006a). The radioactive disequilibrium of a regolith is function of time and weathering intensity (Dosseto et al., 2008b). Because the radioactive decay of $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ operates at time scales similar to weathering processes, they can be used to estimate rates of regolith production. This is done by modelling the evolution of the U-series isotopic composition of the regolith profile to derive weathering ages, i.e. the time elapsed since the bedrock-forming minerals started to weather (e.g. Chabaux et al., 2011; Dosseto et al., 2011; Dosseto et al., 2012; Dosseto et al., 2008b; Ma et al., 2010; Mathieu et al., 1995; Suresh et al., 2013). The aim is to follow the evolution of the isotopic evolution of mineral phases derived from the parent material through the regolith profile. They can be either residual primary minerals or secondary phases derived from their incongruent dissolution; this ensemble is termed bedrock-derived phases throughout the article. Previous studies have estimated soil production rates on bulk regolith. However, the regolith is a complex mixture of bedrock-derived phases but also solution-derived phases (i.e. produced by precipitation from soil pore water; e.g. iron oxy-hydroxides, carbonates) and organic matter. The presence of the latter two compounds could introduce uncertainties in the model and may result in inaccurate estimation of regolith production rate. To address this potential issue it is necessary to isolate bedrock-derived phases (Suresh et al., 2014). Studies to isolate primary minerals from regolith and sediments have involved sequential extraction procedures (e.g. Blanco et al., 2004; Lee, 2009; Martin et al., 2015; Schultz et al., 1998; Suresh et al., 2010; Tessier et al., 1979). These treatments aim at selectively remove from soil the exchangeable fraction, carbonates, manganese and iron oxides, and organic matter. However, its effect on the U-series isotopic composition of regolith is not clear and needs testing (Blanco et al., 2004; Schultz et al., 1998; Suresh et al., 2014).
In this study sequential extraction and minerals separation (hand-picking of quartz and biotite) are used to isolate bedrock-derived phases from a bulk regolith. The aim is to assess whether the isotopic composition of leached samples and of mineral separates reflect the U-series isotope fractionation of bedrock-derived phases during pedogenesis. To do this, it is needed to remove the influence of solution-derived phases and organic matter. Mineralogical and major element analyses were also performed to better understand the processes at play in the profile and during the sample preparation. The isolation of phases showing an isotopic composition that is not affected by solution-derived phases and organic matter has the potential of improving the current method to estimate regolith production rates using U-series isotopes (Dosseto, 2015; Dosseto et al., 2008b; Suresh et al., 2014).

3.3 Method

3.3.1 Study site & Sample preparation

A weathering profile was sampled from a road cut located on a flat-topped area near Crookwell, NSW Australia (34°26’42.67”S 149°12’1.28”E, 734 AMSL). The soil is a red kandosol, developed on the Silurian Gunning granite formation (Bodorkos S., 2010). A sample of the bedrock was collected from boulders that had been extracted during the road construction; the boulders did not display sign of weathering. The bedrock is mainly composed of quartz, plagioclase and biotite, and small contents of alkali feldspar. Two soil and four saprolite samples were collected at depth of 0.3, 0.9 m and 2.0, 2.2, 2.5 and 2.7 m, respectively (see Appendix C). Samples were dried in an oven at 50 °C, homogenised and divided in three aliquots. The first aliquot was kept untreated, and it is referred to as bulk samples through the rest of the paper. The second aliquot (~ 2 g) underwent sequential extraction, herein referred to as leached samples. Sequential extraction was performed according to Martin et al. (2015), a modified version of the procedure proposed by Tessier et al. (1979). The procedure is composed of four steps destined to selectively remove the exchangeable fraction, carbonates, Mn- and Fe-oxides and organic matter (Table 3.1). In each step, 15 mg of Na(citrate) were added to the sample in order to reduce the re-adsorption of U. At the end of each step, the sample was rinsed twice with water.
The third aliquot was used to separate quartz and biotite from the bulk sample. The aliquot was first wet-sieved and the size fraction greater than 125 μm was retained and dried in an oven at 50 °C. About 10 g of sample were heated at 550 and 950 °C in a furnace for 4 and 2 hr respectively, in order to remove organic matter and carbonates (Heiri et al., 2001). The sample was then treated with 0.04 M NH₂OH·HCl/AcOH (pH 2) at 96 °C for 5 hr, in order to remove U and Th previously bound to organic matter and carbonates, as well as any potential Mn- and Fe-oxide phases precipitated on mineral grains. The sample was then rinsed with H₂O, dried in an oven at 50 °C and quartz and biotite were handpicked under an optical microscope.

3.3.2 U-series, elemental and mineralogical analyses

Mineral quantification was performed on bulk and leached samples by X-ray diffraction, at University of Wollongong. Samples were dried in an oven and crushed with a Tollmill crusher (TEMA) to <4 mm. They were then analysed using a Phillips 1130/90 diffractometer set to 35 kV and 28.8 mA. The analyses were carried out with the following settings: 2-theta between 4 and 70°; 2° per minute and step-size of 0.02. Diffractograms were produced using a GBC-122 control system and analysed using the following softwares: Traces, UPDSM and SIROQUANT.

Major element compositions of bulk and leached samples were determined using fused discs on a Tracor Northern energy dispersive X-ray fluorescence (XRF) analyser with automated, computer-driven data collection and processing, at University of Wollongong. The analytical uncertainty of XRF analyses was estimated using two internal standards and was ±4% for Na₂O, ±20% for SO₃ and ± 1% for the other oxides. Three replicates of bulk samples were analysed to estimate external relative analytical uncertainties (Table 3.3). Because no replicate analysis was performed for samples that undergone sequential extraction, we used the external relative standard error (RSE) estimated for bulk samples. For the loss on ignition (LOI) measurements, approximately 1 g of bulk and leached samples were placed in a crucible and dried in an oven at 105 °C overnight. The LOI measurement were performed at 550 °C for 4 hours following the procedure described in Heiri et al. (2001).
The elemental analysis of quartz separates and the U-series isotopes analysis on bulk and leached aliquots and quartz grains were carried out at the Wollongong Isotope Geochronology Laboratory, University of Wollongong. About 100 mg of homogenized material was weighed and a $^{229}$Th - $^{230}$U tracer solution was added. Samples were dissolved in a mixture of 0.5 ml 70% HClO$_4$ and 2.5 mL of 32% HF at 100 °C overnight. The dissolved samples were dried to incipient dryness in a closed system. This was followed by re-dissolution in 32% HCl and H$_3$BO$_3$ was added when necessary to dissolve residual fluorides. Samples were then heated overnight and dried in a closed system to incipient dryness. They were re-dissolved in concentrated HNO$_3$ and dried to incipient dryness, twice. Finally, they were re-dissolved in 2 mL of 1.5 M HNO$_3$. The resulting solution was separated in two aliquots: ~100 μL were diluted and used for elemental analyses (only for mineral separates), while the rest was used for U-series isotope measurements.

The elemental analyses of quartz and biotite, were performed on an Agilent 7500 Series inductively-coupled plasma mass spectrometer at University of Wollongong (Table 3.4). Concentrations were calculated by external calibration using 8 to 12 standards with concentrations between 0 and 500 ppb for each element of interest. Total procedure blanks for Mg, Ti, Fe and K were ≤1 μg, ≤0.9 μg, ≤5 ng and ≤2 μg respectively, while for Zr it was below the detection limit. Duplicate analyses for one biotite sample was performed to determine external relative analytical uncertainties (RSE). Because replicate analyses of quartz were not possible, we used the external error determined for biotite. The error on replicate analyses is high; this can be explained by heterogeneous concentration of these elements among single quartz and biotite grains.

For U-series isotope measurements, U and Th were separated by solid-liquid chromatography following the procedure described by Luo et al. (1997). The U-series activity ratios and the U and Th concentrations were measured on a ThermoFisher Neptune Plus multi-collector inductively-coupled plasma mass spectrometer at the Research School of Earth Sciences, Australian National University. Standard bracketing was used to correct for SEM-Faraday cup yield and mass bias: for U analyses, synthetic standard CRM U010 was used, while for
Th synthetic standard OU Th’U’ was used. Accuracy of the measurement protocol was assessed using CRM U005A for U and UCSC Th’A’ for Th. Accuracy of the entire procedure (dissolution, U and Th separation, and analysis) was assessed using gravimetric standard QLO-1 (U.S. Geological Survey), which is in secular equilibrium. Measured U and Th concentrations were all within error of the recommended values (Abbey and Canada, 1983; Flanagan and Flanagan, 1976; Govindaraju, 1994) (Table 3.5). The \((^{234}{U}/^{238}{U})\) and \((^{230}{Th}/^{238}{U})\) activity ratios were within 0.3 and 0.4% of secular equilibrium respectively. Total procedure blanks generally ranged between 6 and 87 pg for U, and 3 and 91 pg for Th, except for a period where they ranged 0.1 and 1.4 ng for U and 0.1 and 0.9 ng for Th. However, despite the high blanks, they represented <5% and <0.1% of the average amounts of U and Th analysed. A replicate for one bulk, one quartz and two biotite samples were used to estimate external relative analytical uncertainties (RSE, error bars in Figures 3.4 to 3.6 and Table 3.5). Because replicate analyses for leached samples were not performed, we used the external relative analytical uncertainties of bulk material. As two biotite samples were replicated, we used the highest error. Figures display the average values of the replicates.

### 3.3.3 Mass-transfer coefficients

In a system like a regolith, where all samples are derived from the same parent material, normalising elemental concentrations to an immobile element, \(i\), is useful to estimate elemental gains and losses throughout the profile (Anderson et al., 2002). In bulk and leached samples, and mineral separates the element gains and losses were calculated using the mass-transfer coefficient (\(\tau\)). For an element of interest, \(x\), \(\tau_{i,x}\) is calculated using the equation initially proposed by Nesbitt (1979) and later modified by Anderson et al. (2002):

\[
\tau_{i,x} (%) = \left[\frac{([x/i]_{sample}}{([x/i]_{bedrock}} - 1\right] * 100
\]

(1)

Positive values indicate gain, in percent, of element \(x\) in the sample relative to the bedrock, while negative values indicate loss. This equation was used to calculate the mass-transfer coefficients for Mg, K, Ca, Fe, Al, U and Th (Figures 3.3, 3.4 and 3.5).
For the bulk and leached samples, we identified Ti as relatively immobile element using the intercomponental ratio proposed by Chesworth et al. (1981). Figure 3.1 shows that the ratios among the concentrations of TiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ in bulk and leached samples are constant; this suggests that all three oxides are relatively immobile. This is also confirmed by the increasing oxides concentrations with decreasing depth. We selected Ti as the least mobile element because it has been used in similar studies (e.g. Nesbitt, 1979; Pelt et al., 2008).

![Triangle plot with TiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$](image)

Figure 3.1. Intercomponental ratios for bulk and leached samples reported in a triangular plot (Chesworth et al., 1981). This plot indicates that ratios among TiO$_2$:Al$_2$O$_3$:Fe$_2$O$_3$ are relatively constant, suggesting that all three oxides could be used as relatively immobile elements. However, TiO$_2$ shows smaller variation relative to the other two oxides and was therefore chosen as the least mobile element.

In the biotite separates, Ti is the only element that shows a relatively constant concentration with varying depth (Table 3.3). In contrast, Zr, which is commonly considered immobile, shows decreasing concentrations with depth (Table 3.3). This suggests that Ti is also the least mobile element in the case of biotite.
In quartz separates, Ti concentration increases with decreasing depth, while all the other elements decrease (Zr, K, Na) or vary throughout the profile (Mg, Fe) (Table 3.3). Therefore, Ti is chosen as least immobile element for these samples.

3.4 Results

3.4.1 Bulk samples

The mineralogy of the bedrock is dominated by quartz, plagioclase and biotite (Table 3.2). Magnesium, Al, K, Ca, Fe, U and Th concentrations are similar to the one found in the literature for granitoid rocks (Tables 3.3 and 3.5; Cowart and Burnett, 1994; Harmon and Rosholt, 1982; Rosholt, 1983; Shimizu et al., 2000). The \(^{234}\text{U}/^{238}\text{U}\) activity ratio is within error of secular equilibrium, while the \(^{230}\text{Th}/^{238}\text{U}\) is lower than unity (0.959±0.012).

In the bulk regolith, quartz concentrations vary between 39 and 17% in the profile (Figure 3.2). K-feldspar concentrations increase with decreasing depth, while plagioclases decrease. Biotite content decreases sharply in the lower saprolite relative to the bedrock and remains relatively constant throughout the rest of the profile. Clay concentrations increase with decreasing depth.
In the bulk regolith, K and Ca losses increase with decreasing depth to values up to 69 and 95%, respectively (Figure 3.3). Magnesium loss also increases with decreasing depth, showing constant values in the saprolite (Figure 3.3). In contrast, small losses of Fe are observed throughout the profile and Al varies between gains < 7% and losses < 11% throughout the profile. Finally, Loss on Ignition (LOI) values significantly increase decreasing regolith depth (Table 3.3).

The bulk regolith loses up to ~23 and ~33% of U and Th relative to the bedrock (Figs. 3.4 and 3.5). Thorium is lost during the transfer from the bedrock into the lower saprolite, where it remains relatively constant in the soil. In contrast, loss of U increase continuously in the saprolite, while decrease in the soil. The \(^{234}\text{U}/^{238}\text{U}\) activity ratios decrease with decreasing depth in the saprolite, showing values always lower than unity, and then increase in the soil, up to values greater than one in the upper soil (Figure 3.6). In contrast, the \(^{230}\text{Th}/^{238}\text{U}\) remain nearly constant through the weathering profile, with values slightly lower than 1 (Figure 3.6).
Figure 3.3. Mass-transfer coefficient for K (A), Ca (B), Mg (C), Fe (D) and Al (E) as a function of depth. The dashed line indicates the boundary between saprolite and soil. The error bars are propagated external analytical uncertainties (RSE). In this figure and in the following, if not shown, error bars are within the symbol size.
Figure 3.4 Mass-transfer coefficient for U as a function of depth. The dashed line indicates the boundary between saprolite and soil. The error bars are propagated external analytical uncertainties (RSE).
Figure 3.5. Mass-transfer coefficient for Th as a function of depth. The dashed line indicates the boundary between saprolite and soil. The error bars are propagated external analytical uncertainties (RSE).
Figure 3.6. A) $^{234}\text{U}/^{238}\text{U}$ and B) $^{230}\text{Th}/^{238}\text{U}$ activity ratios in the granitic weathering profile versus depth. The solid lines represent secular equilibrium, while the dashed line indicates the boundary between saprolite and soil.
3.4.2 Leached samples

In the bedrock, sequential extraction results in an apparent enrichment in quartz and K-feldspar and loss of plagioclases and biotite (Figure 3.2). The calculated mass-transfer coefficients show little differences for Mg, K,Ca, Fe and Al when compared to the bulk bedrock (Figure 3.3). In contrast, the leached sample is depleted in U and Th relative to the bulk. Finally, the \( \frac{234\text{U}}{238\text{U}} \) activity ratio is similar between leached and bulk bedrock, while the leached one exhibits a very high \( \frac{230\text{Th}}{238\text{U}} \) activity ratio.

Sequential extraction of saprolite and soil results in an increase in quartz concentrations, a decrease in plagioclases and clays when compared to bulk samples, and does not produce major variations in biotite and K-feldspars (Figure 3.2). Bulk and leached saprolite show similar variation in mass-transfer coefficients for K, Ca, Mg, Fe and Al; although leached samples are systematically depleted in Al compared to the bulk (Figure 3.3). Leached soil show also similar mass-transfer coefficients compared to the bulk; however, the leached samples display an enrichment of Ca and depletions of Mg and Al, compared to the bulk soil. Leached and bulk regolith show similar patterns of evolution for the mass-transfer coefficients of U and Th, and \( \frac{234\text{U}}{238\text{U}} \) activity ratios; although the leached samples displayed more pronounced loss of U and Th, and depletion of \( 234\text{U} \) relative to \( 238\text{U} \) (Figs. 3.4 – 3.6). The \( \frac{230\text{Th}}{238\text{U}} \) activity ratios of the leached regolith show a more irregular pattern compared to the bulk, with values >1 in the mid saprolite and the soil (Figure 3.6).

3.4.3 Quartz

In the bedrock, quartz separates show Ti, K, U and Th concentrations similar to values reported in the literature, while Mg, Fe and Zr concentrations are higher (Tables 3.4 and 3.5; Breiter et al., 2012; Harmon and Rosholt, 1982; Hodson, 2002; Müller et al., 2008; Rusk et al., 2006). The \( \frac{234\text{U}}{238\text{U}} \) and \( \frac{230\text{Th}}{238\text{U}} \) activity ratios are in secular equilibrium (Table 3.5).
In the saprolite, quartz separates show more pronounced depletion in K, Mg and Fe, when compared to the bulk or leached saprolite (Figure 3.3). In contrast, in the soil they show similar τ values for K and Mg, but more pronounced Fe loss.

Quartz separates show a loss of U at the bedrock/saprolite transition, followed by a gradual gain with decreasing depth in the saprolite (Figure 3.4). In the soil, quartz separates show a loss of U compared to the saprolite. The loss of U is more pronounced in the quartz separates compared to bulk and leached regolith. In the saprolite, quartz separates show large enrichment in Th, which contrasts with the Th loss observed in bulk or leached saprolite. However, in the soil, quartz shows Th loss (Figure 3.5). In the quartz separates, the \(^{234}\text{U}/^{238}\text{U}\) and \(^{230}\text{Th}/^{238}\text{U}\) activity ratios show similar patterns of evolution compared to bulk and leached regolith; however, quartz separates show more pronounced depletion in \(^{234}\text{U}\) and \(^{230}\text{Th}\) relative to \(^{238}\text{U}\) (Figure 3.6).

### 3.4.4 Biotite

In the bedrock, the elemental composition of biotite separates is dominated by Mg, K and Fe, which show concentrations of 13, 11 and 28 wt % (Table 3.4). Magnesium, K, Ti, Fe, U and Th concentrations are similar to those reported in the literature, while Zr is higher (Bea et al., 2006; Harmon and Rosholt, 1982; Murphy et al., 1998; Wallander and Wickman, 1999). Similarly to quartz, \(^{234}\text{U}/^{238}\text{U}\) is in secular equilibrium in biotite separates, while \(^{230}\text{Th}/^{238}\text{U}\) is greater than unity (Table 3.5).

Compared to bulk and leached samples, biotite separates show similar pattern of evolution for K mass transfer coefficient, less depletion in Mg and large gains of Fe, U and Th that increase with decreasing depth (Figures 3.3 – 3.5).

Biotite separates show patterns of \(^{234}\text{U}/^{238}\text{U}\) and \(^{230}\text{Th}/^{238}\text{U}\) activity ratios similar to bulk and leached regolith, but they show systematic enrichment in \(^{234}\text{U}\) relative to \(^{238}\text{U}\) (Figure 3.6).
3.5 Discussion

3.5.1 Mineralogical and geochemical evolution with depth of bulk samples

The bulk bedrock is in secular equilibrium for $^{234}\text{U}/^{238}\text{U}$ but not for $^{230}\text{Th}/^{238}\text{U}$ activity ratio, which is less than 1. Similar results have been reported by other authors (e.g. Dosseto et al., 2012; Pelt et al., 2008; Rosholt, 1983). This indicates that the equilibrium between $^{234}\text{U}$ and $^{238}\text{U}$ has not been disturbed. In contrast, the $^{230}\text{Th}/^{238}\text{U} < 1$ can be explain either by addition of U to the bedrock or preferential removal of $^{230}\text{Th}$ relative to $^{238}\text{U}$. Addition of U is an unlikely explanation; because the $^{234}\text{U}/^{238}\text{U}$ of the bedrock equals 1, the U source should have the same isotopic composition. The bedrock sample was collected from an outcrop and the material appeared unweathered; supposedly, U would be added to the rock through water solution which commonly shows different form 1 (Andersen et al., 2009a; Chabaux et al., 2001). In contrast, it is more plausible that the $^{230}\text{Th}/^{238}\text{U} < 1$ is the result of preferential removal of $^{230}\text{Th}$ relative to $^{238}\text{U}$, similarly to what it was observed by Dosseto et al. (2012). Hence it is likely that the bedrock analysed in our study experienced incipient weathering (e.g. weathering rind formation), in which the equilibrium between $^{230}\text{Th}-^{238}\text{U}$ was disrupted, while the $^{234}\text{U}-^{238}\text{U}$ system remained unaffected. Preferential mobilization of $^{230}\text{Th}$ relative to $^{238}\text{U}$ may be the result of the fact that $^{230}\text{Th}$ is located in recoil-tracks produced by alpha decay and may be easily mobilized during early-stage weathering. Thorium-230 is produced by alpha-decay; similarly to $^{234}\text{U}$, these highly energetic reaction can directly eject the newly formed nuclide out the host-grain, or displace it creating a damaged site (recoil-track) in the grain (Kigoshi, 1971). Both these effects enhance $^{230}\text{Th}$ mobility (Gögen and Wagner, 2000; Murakami et al., 1991). The reason why $^{234}\text{U}$ does not display a similar behaviour is unclear.

The mineralogy of bulk samples indicate that biotite and plagioclase are dissolved during regolith development (Figure 3.2). While most biotite is lost during the conversion of the bedrock into saprolite, plagioclases are mostly dissolved in the soil. Clays are increasingly produced with decreasing depth, suggesting that during regolith development primary minerals (biotite and plagioclase) are converted into secondary phases. We observe an
increase in K-feldspar with decreasing depth; this is anomalous, especially when considering the mass-transfer coefficients for K ($\tau_{Ti,K}$), a major component of K-feldspar, which linearly decrease with decreasing depth (Figure 3.3). The slight increase in K-feldspars with decreasing regolith depth reflects faster loss of other minerals, such as biotite and plagioclase which commonly altered more slowly than K-feldspar.

In the bulk regolith, mass-transfer coefficients show that K, Ca, Mg and, to a lesser extent Fe, are lost during regolith development (Figure 3.3); this reflects the dissolution of biotite (which contains significant amount of K), and plagioclase. In contrast, the relative gain and loss of Al do not show a clear trend of variation with depth, suggesting it is immobilised during clay formation. We also observe a gradual loss of U throughout the profile (Figure 3.4). In the saprolite, U is lost during the dissolution of labile primary minerals such as feldspar and biotite. In the soil, U loss is less than in the saprolite, suggesting that some of the U released from the saprolite is immobilised in the soil, probably via adsorption on organic matter. Alternatively, it is possible that U is added to soil by dust deposition. Mass-transfer coefficients for Th ($\tau_{Ti, Th}$) suggest gradual loss of this element with decreasing depth (Figure 3.5). It is possible that, similarly to U, Th is removed during the dissolution of feldspar and biotite.

The bulk regolith profile does not show any signs of elemental gain, except for Al, suggesting little influence from solution-derived phases (e.g. carbonates, Fe oxides) or aerosol inputs.

In the saprolite, ($^{234}\text{U}/^{238}\text{U}$) decreases from unity with decreasing depth (Figure 3.6) illustrating preferential loss of $^{234}\text{U}$ compared to $^{238}\text{U}$ as a result of recoil and/or preferential leaching. The ($^{230}\text{Th}/^{238}\text{U}$) activity ratio is also less than 1, suggesting loss of $^{230}\text{Th}$ relative to $^{238}\text{U}$, also due by recoil and/or preferential leaching from recoil tracks. The depletion of $^{230}\text{Th}$ over $^{238}\text{U}$ is less than that of $^{234}\text{U}$ over $^{238}\text{U}$ suggesting that some of the $^{230}\text{Th}$ released may be re-adsorbed on the saprolite components.

In the soil, the gain of U suggests U uptake characterized by ($^{234}\text{U}/^{238}\text{U}$) > 1.
Major element analyses indicate no addition of other elements (hence minerals) to the soil; this suggests that the U gained in this horizon is probably derived from solutions and originates in the saprolite. The observation of \( (^{234}\text{U}/^{238}\text{U}) <1 \) in the saprolite supports the hypothesis that the solution interacting with the saprolite would have a \( (^{234}\text{U}/^{238}\text{U}) >1 \). If U from this solution is transferred upward by groundwater and adsorbed onto organic matter in the soil, it would imprint a \( (^{234}\text{U}/^{238}\text{U}) >1 \). This mechanism was first hypothesised by Rosholt et al. (1966), who observed similar U concentrations and \( (^{234}\text{U}/^{238}\text{U}) \) activity ratio variations with regolith depth. Alternatively, it is possible that a small amount of U, characterized by \( (^{234}\text{U}/^{238}\text{U}) >1 \), is added to the soil via dust deposition. Indeed, dust particles showing \( (^{234}\text{U}/^{238}\text{U}) >1 \) have been observed by Pelt et al. (2013). Moreover, the soil displays a moderate concentration of U; a small amount of U added by dust may result in the observed increase in \( (^{234}\text{U}/^{238}\text{U}) \) and may not significantly modify major element concentrations. The \( (^{230}\text{Th}/^{238}\text{U}) \) in the soil is comparable to that in the saprolite, suggesting loss of \(^{230}\text{Th} \) by recoil, with a fraction possibly re-adsorbed on soil particles.

### 3.5.2 The effect of sequential extraction

When comparing leached and bulk bedrock, we observe little differences in mass-transfer coefficients for major elements. This suggests that mineral phases are mostly unaffected by sequential extraction. However, we observe a significant loss of U and Th after leaching. This is accompanied by a large increase in \( (^{230}\text{Th}/^{238}\text{U}) \), and \( (^{234}\text{U}/^{238}\text{U}) \) to a lesser extent. This reflects the release of a pool of U and Th depleted in \(^{230}\text{Th} \) and \(^{234}\text{U} \), during sequential extraction. The observations could reflect the release of U and Th at grain boundaries and/or inclusions. Picciotto (1950) showed that in granites, a significant amount of U-series isotopes are stored at grain boundaries. Tilton et al. (1955) found that U and Th contained in grain boundaries of a granite can be removed by a weak acid leach (6 M HCl at room temperature). Similar results were also confirmed by Pliler and Adams (1962). As during sequential extraction samples are leached at pH as low as 2 and at temperature up to 96°C, it is likely that this treatment mobilizes U and Th in grain boundaries and/or inclusions, resulting in U and Th losses.
In the saprolite, leached and bulk samples show very similar mass-transfer coefficients for most elements (Figure 3.3). Because sequential extraction aims at removing carbonates, Fe-oxides and organic matter, this suggests that these phases are not significantly present in in the saprolite. In the soil, we observe depletion in Al and enrichment in Ca following sequential extraction (Figure 3.3). This could reflect the breaking down of Al-bearing phases, whereas the mechanism controlling the gain of Ca remains to be explained. Replicate analyses of soil samples indicate that analytical problems for Ca analyses are unlikely (Table 3.3). A possibility is that, only in the two soil samples, Ti is mobilized by sequential extraction, whereas Ca remains immobile. This hypothesis is supported by lower Ti concentrations in leached soils compared to untreated ones, albeit the differences are relatively small. Mobilization of Ti in soil during sequential extraction would result in an underestimation of the loss of other elements.

The LOI measurements indicate that sequential extraction significantly removes organic matter from soil, but not from the saprolite (Table 3.3). This suggests that in the saprolite organic matter could be composed by resistant material that is not dissolved by sequential extraction.

Leached regolith shows significant U and Th depletion when compared to the bulk regolith (Figures 3.4 and 3.5). This suggests that, as in the bedrock, sequential extraction mobilises U and Th not contained in the structure of major mineral phases (since major element are unaffected). Only in the soil, sequential extraction may remove a pool of U and Th contained in the organic matter. The pool of U and Th lost by the saprolite could have been adsorbed from solution onto its components and/or dissolved from grain boundaries and/or inclusions, similarly to the bedrock.

Leached regolith show a pattern in $(^{234}\text{U}/^{238}\text{U})$ variation parallel to that observed in bulk regolith, with lower values for the leached regolith (Figure 3.6). This can be explained if the U removed during sequential extraction has a constant $(^{234}\text{U}/^{238}\text{U})$, greater than that of the bulk regolith. This could be U adsorbed onto regolith mineral components from regolith pore water, which is expected to be characterized by a $(^{234}\text{U}/^{238}\text{U}) > 1$. 

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In most cases, \(^{230}\text{Th}/^{238}\text{U}\) in the leached regolith is greater than that in the bulk regolith (Figure 3.6). This suggests that during sequential extraction \(^{238}\text{U}\) is preferentially lost over \(^{230}\text{Th}\). This is supported by trace element data, as we observe that the loss of \(U\) is greater than the loss of \(Th\) (Figures 3.4 and 3.5). The pool of nuclides removed by sequential extraction may have been adsorbed form pore water onto regolith components (minerals and/or organic matter).

Overall, even if sequential extraction does not affect major mineral phases, it seems to mobilize \(U\) and \(Th\), whether in the bedrock or in the regolith. It is possible that a pool of bedrock-derived \(U\) and \(Th\) is removed for instance from grain boundaries and/or inclusions; in such a case artificial radioactive disequilibrium would be created in leached samples. As a result, we do not recommend the use of sequential extraction on granitic weathering profiles.

### 3.5.3 Mineral separates

In the bedrock, quartz is in secular equilibrium for both isotopic ratios. In contrast, while biotite also shows \(^{234}\text{U}/^{238}\text{U}\) in secular equilibrium, it is enriched in \(^{230}\text{Th}\) relative to \(^{238}\text{U}\). It is possible that during mineral separation, which involves a chemical leach, unfractionated \(U\) (characterized by \(^{234}\text{U}/^{238}\text{U}\) =1) was preferentially released relative to \(^{230}\text{Th}\). This would agree with what we observed during sequential extraction of the bedrock, which showed a release of a pool of \(U\) and \(Th\) significantly depleted in \(^{230}\text{Th}\) relative to \(^{238}\text{U}\). Alternatively, it is possible that, in the bedrock, biotite has a \(^{230}\text{Th}/^{238}\text{U}\) >1; in this case the process determining this isotopic composition in the bedrock remains unknown.

The mass-transfer coefficients for \(K\), \(Mg\), \(Fe\), \(U\) and \(Th\) were calculated for biotite and quartz separates. In the regolith, quartz separates show an extensive loss of \(K\), \(Mg\), \(Fe\) and \(U\) (Figure 3.3). A pool of these elements is removed from quartz surfaces and/or inclusions, during weathering (Adams, 1959; Dosseto, 2015; Zielinski et al., 1982). In contrast, we observe a gain of \(Th\) in the saprolite quartz (Figure 3.5), possibly reflecting adsorption onto the mineral surface (Misaelides et al., 2001). Alternatively, it is possible that during the conversion of
the bedrock into the saprolite, Ti is more mobile than Th, resulting in an apparent gain of Th. This hypothesis is unlikely because, as opposed to Th concentrations which increases in the saprolite quartz and decrease in soil quartz, Ti concentrations show a linear increase with decreasing depth, suggesting that Ti is relatively immobile. If Ti was significantly mobilized from quartz during pedogenesis, its concentrations would not increase with decreasing regolith depth. In contrast, in soil, quartz shows a loss of Th; which can be explained by its greater mobility in the presence of organic material (Chabaux et al., 2003). Loss on ignition measurements on bulk material showed that the soil contains significant amount of organic matter, which could increase Th mobility and favour its removal from this horizon. The same is not true for the saprolite, which contains little organic matter.

Quartz shows variations in (234U/238U) and (230Th/238U) with depth parallel to those observed in the bulk or leached regolith. In the saprolite, quartz shows (234U/238U) and (230Th/238U) <1 suggesting that 234U and 230Th are preferentially lost over 238U (possibly from grain boundaries and/or inclusions) as a result of recoil and/or preferential leaching from recoil tracks. Note that the loss of 230Th relative to 238U is not consistent with the mass-transfer coefficients for U and Th. In quartz separated from the saprolite we hypothesized Th gain and U loss. Indeed, Th gain implies adsorption of 232Th (the most common isotope of Th) and not necessarily 230Th. The mechanism to explain preferential adsorption of 232Th relative to 230Th on quartz grains remains to be explained. In the topsoil, (234U/238U) and (230Th/238U) ratios are still <1 but greater than in the saprolite. This could reflect an uptake of 234U and 230Th. The source of U enriched in 234U relative to 238U could be the soil pore water, which is commonly characterized by (234U/238U) >1 (Andersen et al. 2009). In the bulk regolith, we observed (230Th/238U) <1 and hypothesised that 230Th is preferentially removed relative to 238U and released into solution by recoil and/or preferential leaching from recoil tracks (see section 4.1). We also proposed that a fraction of the removed 230Th may be re-adsorbed onto soil particles; hence, quartz may represent an example of this process.

Overall, quartz could be considered as a mineral separate to study regolith formation and particularly U-series isotope fractionation, although it is subject to the uptake of nuclides.
Nuclides adsorbed onto quartz surface may not be removed by the protocol used in this experiment, i.e. ignition at 550 and 950 °C followed by 0.04 M NH₂OH·HCl/AcOH (pH 2) leach at 96 °C. In this case, a strong-acid leach (e.g. using solutions containing different concentrations of HCl and/or HNO₃) could complete the removal; this could be assessed in further studies.

The biotite separates show a loss of K and Mg in the regolith (Figure 3.3), very similar to the losses observed in the bulk and leached regolith. This suggests that most of the loss in K and Mg is accounted for by biotite dissolution. Nevertheless, biotite shows smaller loss of Mg throughout the regolith when compared to the bulk samples (Figure 3.3). This suggests that, during pedogenesis, Mg loss is not controlled only by biotite dissolution but also by the weathering of other mineral phases. Biotite is showing a gain of Fe, probably adsorbed onto this mineral during pedogenesis. A fraction of the adsorbed Fe may originate from inclusion and/or impurities in quartz, as the mineral separates show a greater loss of Fe compared to bulk regolith (Figure 3.3). Biotite also shows a gain of U throughout the profile (Figure 3.4), suggesting an uptake of U possibly originated from the dissolution of other phases present in the regolith. Few studies have described the adsorption of U onto biotite (e.g. Idemitsu et al., 1994; Ilton et al., 2004; Lee et al., 2009a; Lee et al., 2009b). In granitic biotite, U is adsorbed predominantly via redox reactions, in which mobile U(VI) is converted to less mobile U(IV); the reaction is controlled by chemical composition of the biotite and the aqueous solution (pH, alkali cations concentration; Ilton et al., 2004). In the case of our samples, it is possible that U released in solution from other minerals during weathering is adsorbed onto biotite. In other words, biotite acts as a sponge towards U.

Similarly to U, biotite shows a continuous gain of Th throughout the profile (Figure 3.5). Misaelides et al. (2001) studied the interaction between dissolved Th and biotite; they concluded that Th in aqueous solution is adsorbed on the surface of this mineral. Therefore, the results indicate that biotite uptakes U and Th during pedogenesis.
In the regolith, biotite separates show \( \frac{^{234}U}{^{238}U} > 1 \), suggesting that the U adsorbed onto this mineral has \( \frac{^{234}U}{^{238}U} > 1 \) and that it likely derives from soil pore water. The \( \frac{^{230}Th}{^{238}U} \) activity ratios greater than 1 (Figure 3.6) suggest that \(^{230}\text{Th}\) is gained preferentially over \(^{238}\text{U}\), in agreement with the very large gain of Th observed (Figure 3.5).

Overall, biotite acts as a “sponge” for U and Th and thus is not recording the weathering of bedrock-derived phases. As a result, it is not recommended as a mineral separate to study regolith formation.

### 3.6 Conclusions

Sequential extraction and mineral separation were tested to assess if they minimize the effect of solution-derived phases and organic matter on the U-series isotopic composition of a granitic regolith profile. The aim is to study the isotopic evolution of bedrock-derived phases throughout the profile.

In the bulk saprolite, U and Th are mobilized during pedogenesis and \(^{234}\text{U}\) and \(^{230}\text{Th}\) are preferentially removed relative to \(^{238}\text{U}\). The pool of U and Th mobilized originates from the dissolution of labile bedrock-derived minerals, such as feldspars and biotite. In contrast, in the bulk soil U and Th seem to be gained from solution, and \(^{234}\text{U}\) and \(^{230}\text{Th}\) are preferentially adsorbed relative to \(^{238}\text{U}\).

Sequential extraction is expected to remove secondary phases, such as Fe-oxide, carbonates and the exchangeable fraction (e.g. adsorbed phases), and organic matter from regolith samples. In the bedrock, sequential extraction does not dissolve major minerals. However, it removes U and Th, possibly from grain boundaries and/or inclusions. Similarly to what is observed for the bulk regolith profile, \(^{234}\text{U}\) and \(^{230}\text{Th}\) are preferentially mobilized relative to \(^{238}\text{U}\). In the regolith, sequential extraction does not remove the expected phases (e.g Fe-oxide and carbonates); nevertheless, it removes pools of U and Th. The data indicate that the pool of U removed has constant \( \frac{^{234}U}{^{238}U} \), whereas the treatment preferentially removes \(^{238}\text{U}\) than \(^{230}\text{Th}\). It is possible that the pool of U and Th removed by sequential extraction is located in phases that have precipitated from pore water onto minerals surfaces. Alternatively, it is
dissolved from grain boundaries and/or inclusions. As the pool of U and Th could be bedrock-derived, we do not recommend using sequential extraction in this weathering profile.

Quartz separates show loss of U throughout the regolith, whereas Th is gained in the saprolite and removed from the soil. The pool of U and Th mobilized may reside in grain boundaries and/or inclusions. In the saprolite, quartz shows $\left( ^{234}\text{U}/^{238}\text{U} \right)$ and $\left( ^{230}\text{Th}/^{238}\text{U} \right) < 1$, indicating that, during pedogenesis, $^{234}\text{U}$ and $^{230}\text{Th}$ are preferentially mobilized relative to $^{238}\text{U}$ by recoil and/or preferential leaching from recoil tracks. In the top soil, $\left( ^{234}\text{U}/^{238}\text{U} \right)$ and $\left( ^{230}\text{Th}/^{238}\text{U} \right)$ show little increase which may indicate the presence of U-series isotopes adsorbed from solution. As a result, quartz isotopic composition throughout a weathering profile is suitable to study U-series nuclides fractionation during pedogenesis. However, it is necessary to develop a method to remove possible nuclides adsorbed onto quartz surface to minimize the influence of solution-derived nuclides.

Biotite separated from the regolith adsorbs U and Th characterized by $\left( ^{234}\text{U}/^{238}\text{U} \right)$ and $\left( ^{230}\text{Th}/^{238}\text{U} \right) > 1$. These elements are likely to be adsorbed from water solution and may originate from weathering of other minerals in the regolith such as quartz. Biotite acts as a “sponge” for U-series isotopes; hence it is not suitable to study regolith formation and the U-series isotope fractionation occurring during this process.

This study suggests that mineral separation is a promising pre-treatment for the study of U-series isotopes in weathering profiles. In contrast, sequential extraction may not remove only Fe-oxides, carbonates and organic matter, but also bedrock-derived phases such as mineral inclusions, resulting in artificial radioactive disequilibrium.
Table 3.1. Sequential extraction procedure used in this study and target phases. All reagent volumes are intended for 1 g of sample.

<table>
<thead>
<tr>
<th>Phase aimed at</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Exchangeable</td>
<td>8 mL of 1 M Mg(NO₃)₂. Agitate at room temperature for 50 min.</td>
</tr>
<tr>
<td>(2) Acid-soluble</td>
<td>16 mL of 1 M NaOAc at pH 5 (adjusted with AcOH). Agitated at room temperature for 5 hr.</td>
</tr>
<tr>
<td>(3) Reducible</td>
<td>20 mL 0.04M NH₂OH·HCl/AcOH (pH 2). At 96 °C for 5 hr and agitated occasionally.</td>
</tr>
<tr>
<td>(4) Oxidisable</td>
<td>- 3 mL of 0.02 M HNO₃ + 5 mL 30% H₂O₂ at pH 2 (adjusted with HNO₃), at 85 °C for 2 hr and occasionally agitated.</td>
</tr>
<tr>
<td></td>
<td>- 3 mL 30% H₂O₂, pH 2 (adjusted with HNO₃), at 85 °C for 3 hr and occasionally agitated.</td>
</tr>
<tr>
<td></td>
<td>- 5 mL of 3.2 M NH₄OAc in 20% HNO₃, diluted up to 20 mL with H₂O, agitated at room temperature for 30 min.</td>
</tr>
</tbody>
</table>
Table 3.2 Mineralogical concentrations for the bulk and leached samples expressed as wt %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Quartz</th>
<th>K-feldspar</th>
<th>Plagioclase</th>
<th>Biotite</th>
<th>Titanite</th>
<th>Clays</th>
<th>Total</th>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>16.7</td>
<td>18.8</td>
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<td></td>
<td>50.5</td>
<td>100</td>
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<td>100</td>
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<td>2.8</td>
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<td></td>
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</tr>
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<td>Al₂O₃</td>
<td>SiO₂</td>
<td>P₂O₅</td>
<td>SO₃</td>
<td>K₂O</td>
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<td>0.04</td>
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<td>0.04</td>
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<td>0.03</td>
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</tr>
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**External relative analytical uncertainties (RSE)**  
±2.5%  ±2.6%  ±0.66%  ±0.29%  ±39%  ±7.04  ±1.3%  ±0.52%  ±1.5%  ±1.8%  ±1.6%  ±4.4%

The reported external relative analytical uncertainties (RSE) were calculated as the standard error of the average of duplicates measurements for three bulk samples.
Table 3.4. Sodium, Mg, Ti, Fe, K, Al and Zr concentrations in biotite (in wt.% and ppm) and quartz (in ppm) separates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Na2O wt.% SD</th>
<th>MgO wt.% SD</th>
<th>TiO2 wt.% SD</th>
<th>Fe2O3-T SD</th>
<th>K2O wt.% SD</th>
<th>Zr ppm SD</th>
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</thead>
<tbody>
<tr>
<td>Biotite</td>
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<td></td>
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</tr>
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<th>Mg ppm</th>
<th>SD</th>
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<th>SD</th>
<th>K ppm</th>
<th>SD</th>
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<td>0.42</td>
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<td>GR01 H9</td>
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<td>921</td>
<td>13</td>
<td>59.2</td>
<td>0.9</td>
<td>96.6</td>
<td>1.8</td>
<td>343.3</td>
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<td>4.42</td>
<td>0.04</td>
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<td>46</td>
<td>53.7</td>
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<td>85.5</td>
<td>0.8</td>
<td>310.6</td>
<td>6.1</td>
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<td>0.03</td>
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<td>GR01 H11</td>
<td>2.5</td>
<td>1569</td>
<td>19</td>
<td>37.0</td>
<td>0.5</td>
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<td>258.0</td>
<td>4.4</td>
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<td>81.0</td>
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<td>1.68</td>
<td>0.01</td>
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<td>1.2</td>
<td>754.3</td>
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<td>20.6</td>
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Estimated external relative analytical uncertainties (RSE)

<table>
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<tr>
<th>Sample</th>
<th>Na ppm</th>
<th>Mg ppm</th>
<th>Ti ppm</th>
<th>Fe ppm</th>
<th>K ppm</th>
<th>Zr ppm</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>±24%</td>
<td>±20%</td>
<td>±3.2%</td>
<td>±14%</td>
<td>±19%</td>
<td>±8.7%</td>
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</tbody>
</table>

The reported external relative analytical uncertainty (RSE) was calculated as the standard error of the average of the duplicate measurement of two biotite samples.
Table 3.5. U-series isotopes analyses of digested bulk and leached samples, quartz and biotite.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Sample</th>
<th>Depth (m)</th>
<th>Th (ppm)</th>
<th>2SE (U (ppm))</th>
<th>2SE (238U/238U)</th>
<th>2SE (230Th/238U)</th>
<th>2SE (234U/230Th)</th>
<th>2SE (230Th/232Th)</th>
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<tr>
<td>Bulk</td>
<td>GR01H3</td>
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<td>1.025</td>
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<tr>
<td></td>
<td>GR01H6</td>
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<tr>
<td></td>
<td>GR01H9</td>
<td>2</td>
<td>20.3</td>
<td>0.04</td>
<td>1.89</td>
<td>0.01</td>
<td>0.912</td>
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<tr>
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<td>0.945</td>
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<td>0.987</td>
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<td></td>
<td>GR01 Bedrock rep1</td>
<td>3</td>
<td>13.33</td>
<td>0.02</td>
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<td>0.01</td>
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<td>3</td>
<td>31.6</td>
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<tr>
<td>Sequential</td>
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<td>leaching</td>
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<td>1.016</td>
<td>0.002</td>
<td>2.128</td>
</tr>
</tbody>
</table>

External relative analytical uncertainties (RSE): ±29 ±4.4% ±0.14% ±2.1% ±25% ±27%

| Biotite           | GR01H6            | 0.9       | 68.95    | 0.09          | 3.93            | 0.04            | 1.016           | 0.008             | 1.139|
|                   | GR01H9 Biotite rep1 | 2    | 35.13    | 0.08          | 3.39            | 0.04            | 0.962           | 0.007             | 0.941|
|                   | GR01H9 Biotite rep2 | 2    | 36.47    | 0.08          | 3.42            | 0.05            | 0.948           | 0.007             | 0.851|
|                   | GR01H10           | 2.2       | 45.46    | 0.09          | 3.18            | 0.03            | 1.026           | 0.006             | 1.024|
|                   | GR01H11           | 2.5       | 58.64    | 0.18          | 2.91            | 0.03            | 1.111           | 0.008             | 1.396|
|                   | GR01H12 rep1      | 2.7       | 31.32    | 0.05          | 2.17            | 0.02            | 1.129           | 0.01              | 1.275|
|                   | GR01H12 rep2      | 2.7       | 30.38    | 0.04          | 2.1             | 0.02            | 1.113           | 0.006             | 1.175|
|                   | GR01 Bedrock      | 3         | 1.07     | 0            | 0.86            | 0.01            | 1.009           | 0.009             | 1.139|

External relative analytical uncertainties (RSE): ±1.3% ±0.26% ±0.50% ±3.5% ±1.1% ±4.6%

159
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<td>0.005</td>
<td>1.64</td>
<td>0.004</td>
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<td>0.006</td>
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</tbody>
</table>

External relative analytical uncertainties (RSE) ±2.7% ±8.5% ±0.18% ±1.3% ±11% ±9.8%

| Gravimetric standard | QLO-1 (average n=5) | 4.7 | 0.01 | 1.83 | 0.01 | 1.003 | 0.005 | 1.004 | 0.017 | 1.183 | 0.011 | 1.186 | 0.012 |

The reported external relative analytical uncertainties (RSE) were calculated as the standard error of the average of duplicates measurements for on bulk sample, one biotite and one quartz separate. Gravimetric standards are presented as an average (n=5) and the standard error is calculated as the propagated standard error of all measurement.
References


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Murphy, R.J., Lenhart, J.J., Honeyman, B.D., 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. Colloids and surfaces A: physicochemical and engineering aspects 157, 47-62.


4 Sequential extraction and quartz separation to study U-series isotopes fractionation in a podzol

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4.1 Abstract

In a weathering profile, the trend of variation of the uranium-series (U-series) isotopic composition with depth can be modelled to estimate regolith production rates. In bulk regolith, the presence of secondary phases and organic matter (OM) may introduce uncertainties in the model and decrease the accuracy of regolith production rates. A pre-treatment to isolate phases derived from the bedrock could address this drawback.

Here, we investigate the U-series isotopic composition of a Podzol developed on sandstone. Sequential extraction and mineral separation of quartz are tested as pre-treatments to isolate phases derived from the bedrock and the isotopes associated with them. Major element and U-series isotopic composition is used to understand processes at play during regolith development and after sequential extraction and mineral separation.

In the bulk regolith, mineralogical, major element and U-series isotopic analyses indicate that U and Th are eluviated from the E horizon and illuviated into the B horizon, where they are likely retained in secondary phases and organic matter.

Sequential extraction is a chemical method to selectively remove secondary phases and organic matter from soil. In this profile, sequential extraction does not affect the E horizon; this is because secondary phases and organic matter are not significantly present due to eluviation processes. In the B horizon, it removes, at least partially, the illuviated U-series isotopes associated with secondary phases and organic matter. This treatment could improve the accuracy of regolith production rates inferred using U-series isotopes.

In quartz separates, the data indicate continuous loss of U and Th with decreasing regolith depth, whereas no evidence suggests gain of U and/or Th. Quartz records the fractionation of U-series isotopes during regolith formation and could be a candidate mineral to estimate regolith production rates (quartz residence time in regolith). The U and Th released from quartz may be stored in mineral impurities and/or inclusions.
4.2 Introduction

Uranium-series (U-series) isotopes are present in rock-forming minerals and fractionate during weathering processes and regolith development. Because they undergo radioactive decay with half-lives comparable to weathering timescales (thousands to millions of years), they can be used to quantify timescale of Earth surface processes such as regolith production rates (Chabaux et al., 2003; Dosseto et al., 2008a; Ivanovich and Harmon, 1992; Vigier et al., 2001).

Studies of Earth surface processes commonly focus on three isotopes: $^{238}$U, $^{234}$U and $^{230}$Th. A system, such as a bedrock, that has remained closed for more than ~1 Myr will be in secular equilibrium, namely when all isotopes show equal activities (Bourdon et al., 2003). In such a case, the bedrock will display $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ equal to 1, where parenthesis denote activity ratios throughout this article. When weathering takes place, isotopes fractionate because of their different mobility, which is expected to be $^{234}\text{U} > ^{238}\text{U} > ^{230}\text{Th}$ (Chabaux et al., 2003). As a result, in the regolith, residual primary minerals are expected to show $(^{234}\text{U}/^{238}\text{U}) < 1$ and $(^{230}\text{Th}/^{238}\text{U}) > 1$, whereas the weathering solution will be enriched in the more mobile isotopes and will show $(^{234}\text{U}/^{238}\text{U}) > 1$ and $(^{230}\text{Th}/^{238}\text{U}) < 1$ (Andersen et al., 2009a; Chabaux et al., 2008). During pedogenesis, complex processes of elements redistribution may occur throughout the regolith (e.g. eluviation/illuviation), as well as addition of elements transported by water solution (e.g. co-precipitation of U and Fe-oxides) and dust (e.g. Andersen et al., 2013; Duff et al., 2002; Pelt et al., 2013). Because the aqueous solution normally shows $(^{234}\text{U}/^{238}\text{U}) < 1$ and $(^{230}\text{Th}/^{238}\text{U}) > 1$, solution-derived phases (e.g. Fe-oxides) will display analogous isotopic composition (Plater et al., 1992). Similarly, organic matter is known to adsorb U-series isotope from the aqueous solution and it is expected to show $(^{234}\text{U}/^{238}\text{U}) > 1$ and $(^{230}\text{Th}/^{238}\text{U}) < 1$ (Ames et al., 1983a; Chabaux et al., 2003).

Dequincey et al. (2002) proposed a model, later modified by Dosseto et al. (2008b), to estimate regolith production rates by measuring the U-series isotopic composition of a weathering profile at different depths. To date, most regolith production rates inferred using U-series isotopes have been assessed on bulk regolith; hence minerals derived from the bedrock, as well as secondary phases and organic matter were included in samples.
(Chabaux et al., 2013; Dequincey et al., 2002; Dosseto et al., 2011; Dosseto et al., 2012; Dosseto et al., 2008b; Gontier et al., 2015; Ma et al., 2010; Ma et al., 2013; Mathieu et al., 1995). Throughout this article, the ensemble of all phases present in the regolith that are derived from the bedrock (i.e. residual primary minerals and clays produced as a result of incongruent dissolution of primary minerals) is referred to as bedrock-derived phases. Phases precipitated from solution are referred to as solution-derived phases.

Conceptually, the model from which regolith production rates are derived assumes that regolith is formed by the downward migration of the weathering front through the bedrock (Dosseto et al., 2012). The model reconstructs the isotopic evolution of a regolith with depth, from the time U-series isotopes started fractionating as a result of weathering at the bedrock-saprolite interface. It then returns regolith production rates (Dosseto et al., 2008b). Two central assumptions are made by the model. Firstly, during regolith formation bedrock-derived phases undergo continuous loss of U-series isotopes due to mineral dissolution. This assumption reflects weathering processes and suggests that regolith production rates estimated by the model are integrated through time and represent an averaged value. Secondly, during pedogenesis U-series isotopes are constantly gained by the regolith due to precipitation of solution-derived phases—for instance, due to illuviation—and dust and organic matter deposition (Dosseto et al., 2012; Dosseto et al., 2008b). However, loss and gain of U-series isotopes during pedogenesis may operate at different timescales; Dosseto et al. (2012) identified this as a drawback of the model which could result in inaccurate regolith production rates. Treatments to eliminate solution-derived phases and organic matter from regolith and/or isolation of bedrock-derived minerals are methods that could improve the accuracy of the model from which regolith production rates are estimated, when compared to rates inferred from bulk material (Dosseto, 2015). For instance, by eliminating solution-derived phases and organic matter from regolith, the model could be simplified by removing the assumption of continuous gain of nuclides due to precipitation of solution-derived phases and organic matter. Alternatively, U-series analyses of bedrock-derived phases isolated from regolith can be modelled to quantify the time elapsed since phases started weathering at the bedrock-saprolite interface, i.e. mineral residence time in the regolith (Dosseto et al., 2008b).
Here, we test two approaches to isolate bedrock-derived phases (suggested by Dosseto, 2015): i) sequential extraction, a method to chemically separate different phases in soil and that can be used to remove solution-derived phases and organic matter (Schultz et al., 1998; Tessier et al., 1979); and ii) mineral separation of quartz by hand-picking. The aim is to assess whether sequential extraction and/or mineral separation isolates bedrock-derived minerals and if the U-series isotopic composition of leached samples and mineral separates is affected by solution-derived phases and/or organic matter.

While the possibility of estimating regolith production rates on mineral separates has not been tested, few studies have investigated the effect of sequential extraction on the U-series isotopic composition of bulk regolith (Lee, 2009; Martin et al., 2015; Suresh et al., 2014). Suresh et al. (2014) applied sequential extraction to a soil sample and observed a loss of U and Th, accompanied by variation of (234U/238U) and (230Th/238U) activity ratios relative to the bulk sample. The authors could not determine which mineral phases were removed by sequential extraction and could not assess if the pool of U and Th removed was retained in solution-derived phases, organic matter and/or bedrock-derived phases. In another study, Martin et al. (2015) applied sequential extraction to a soil and suggested that non-detrital material (e.g. solution-derived phases and organic matter) was removed from the sample. Similarly to the study mentioned above, Martin et al. (2015) focused on top soil material, whereas the rest of the regolith profile was not examined. In this experiment, we study the effect of sequential extraction and mineral separation on a podzol, monitoring variations in mineralogical, major elements and U-series isotopic compositions.

4.3 Methods

4.3.1 Site description

The study area is situated in Tolwong in the Southern Highlands, New South Wales, Australia (34°51'37.80"S, 150° 7'40.35"E). The mean annual rainfall is 827 mm. The regolith profile is located on a upland; the area is mostly covered by natural open woodland and partially used for animal breeding. The bedrock is a Permian sandstone and is overlain by a weathering profile classified as a Podzol or Kurosol by the Australian Soil Resource Information System (Johnston et al., 2003; Laffan et al., 1998; Rose, 1966).
The upper 10-15 cm are rich in litter and non-decomposed organic material (O horizon) and overlay a light, grey-coloured E horizon which extends to a depth of approximately 50 cm. Between 50 and 130 cm, the colour turns to reddish-brown, indicating illuviation of organic matter and secondary minerals (B horizon). Below 130 cm we observed a gradual transition toward the saprolite, but could not drill deeper than 1.8 m of depth. A core was collected using a mechanical sampler (see picture in Appendix C) and samples were extracted as follows: two samples were collected from the E horizon at 20 and 40 cm, and other two were sampled from the B horizon at 130 and 180 cm. The bedrock was sampled from a nearby outcrop. In the weathering profile, bedrock depth has been estimated to be between 3 and 10 m by the Terrestrial Ecosystem Research Network (TERN) initiative of Government of Australia (see http://tern.org.au).

4.3.2 Sample preparation, sequential extraction and mineral separation

After drying in an oven at 50 °C, samples were homogenised and separated in three aliquots. The first aliquot was kept untreated and is referred to as bulk throughout the rest of the article. The second aliquot (~ 2 g) underwent sequential extraction, herein referred to as leached samples, while the third was used to separate quartz grains.

The sequential extraction procedure is composed by five steps and was performed according to Martin et al. (2015; Table 4.1). Before each step, ~15 mg of sodium citrate were added to the sample to reduce U and Th re-adsorption onto the solid residue. At the end of each step, the sample was rinsed twice with deionized water.

The aliquot intended for quartz separation was wet-sieved and the size fraction greater than 125 μm was retained and dried in an oven. To facilitate handpicking of quartz, organic matter and carbonates were removed by heating ~10 g of sample at 550 and 950 °C in a furnace for 4 and 2 hr, respectively (Heiri et al., 2001). In order to remove U and Th previously bound to organic matter and carbonates, as well as Mn- and Fe-oxides, samples were leached with 0.04 M NH₂OH·HCl/AcOH (pH 2) at 96 °C for 5 hr. Finally, the residues were rinsed twice with deionized water and quartz was hand-picked under a microscope.
Table 4.1. Sequential extraction procedure and targeted phases. All reagent volumes are intended for 1 g of sample.

<table>
<thead>
<tr>
<th>Phase removed</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>8 mL of 1 M Mg(NO3)2. Agitate at room temperature for 50 min.</td>
</tr>
<tr>
<td>Carbonates</td>
<td>16 mL of 1 M NaOAc at pH 5 (adjusted with concentrated AcOH). Agitated at room temperature for 5 hr.</td>
</tr>
<tr>
<td>Fe- and Mn-oxides</td>
<td>20 mL 0.04M Nh2OH·HCl/AcOH (pH 2). At 96 °C for 5 hr and agitated occasionally.</td>
</tr>
<tr>
<td>Oxidisable</td>
<td>- 3 mL of 0.02 M HNO3 + 5 mL 31% H2O2 at pH 2 (adjusted with concentrated HNO3), at 85 °C for 2 hr and occasionally agitated.</td>
</tr>
<tr>
<td></td>
<td>- 3 mL 31% H2O2, pH 2 (adjusted with concentrated HNO3), at 85 °C for 3 hr and occasionally agitated.</td>
</tr>
<tr>
<td></td>
<td>- 5 mL of 3.2 M NH4OAc in 20% HNO3, diluted up to 20 mL with H2O, agitated at room temperature for 30 min.</td>
</tr>
</tbody>
</table>

4.3.3 Mineralogical, elemental and U-series analyses

Mineralogical analyses were performed on bulk aliquots by X-ray diffraction (XRD) at University of Wollongong. First, the samples were dried in an oven and grounded to <4 μm using a Tollmill crusher (TEMA). The powdered samples were analysed on a Phillips 1130/90 diffractometer with the following settings: 35 kV, 28.8 mA, 2-theta range between 4 and 70°; 2° per minute and step-size of 0.02. A GBC-122 control system was sued to obtain the diffractograms, which were processed using the three softwares Traces, UPDSM and SIROQUANT.

Bulk and leached samples were analysed for major elements as fused discs on a Tracor Northern energy dispersive X-ray fluorescence (XRF) analyser with automated, computer-driven data collection and processing, at University of Wollongong. Two internal standards were used to estimate analytical uncertainties and was ±4% for Na2O,
±20% for SO$_3$ and ± 1% for the other oxides. A duplicate of the bulk bedrock was used to determine external analytical uncertainties (Table 4.3). No duplicate analyses were performed on the leached material; we used the relative external analytical uncertainties estimated for bulk samples. The loss on ignition (LOI) measurements were performed on approximately 1 g of bulk and leached samples. Samples were placed in a crucible and dried in an oven at 105 °C overnight. The LOI measurement were performed at 550 °C for 4 hours following the method proposed by Heiri et al. (2001).

Elemental analysis on quartz separates and U-series isotopic analyses on bulk and leached aliquots and quartz grains were carried out on acid-dissolved samples, which were prepared at the Wollongong Isotope Geochronology Laboratory, University of Wollongong. Approximately 100 mg of sample were weighed and a tracer solution containing $^{229}$Th - $^{236}$U was added before dissolution. Samples were treated with 0.5 mL 69% HNO$_3$ and 2.5 mL of 32% HF at 100 °C overnight and, once dissolved, they were dried in a closed system. Following this, samples were re-dissolved in 32% HCl and dried in a closed system; H$_3$BO$_3$ was used to dissolve possible residual fluorides. Samples were then re-dissolved in HNO$_3$ twice. Finally, they were taken up in 2 mL of 1.5 M HNO$_3$. For quartz samples, the resulting solution was separated in two aliquots intended for elemental analysis (~100 μL) and U-series isotopes measurements.

Elemental analyses of quartz separates were performed on an Agilent 7500 Series inductively-coupled plasma mass spectrometer at University of Wollongong (Table 4.4). Concentrations were determined by external calibration using 8 – 12 multi-element standards with concentrations between 0 and 500 ppb. External analytical uncertainties were determined by duplicating one sample. Total procedure blanks for Mg, Ti, Fe, and K represented ≤5%, ≤2%, ≤0.01% and ≤4%, respectively, of the average mass analysed in the samples. Zirconium was not detected in total procedure blanks.

For U-series isotopic measurements, U and Th were separated using ion exchange chromatography (Luo et al., 1997). Uranium and thorium concentrations, ($^{234}$U/$^{238}$U) and ($^{230}$Th/$^{238}$U) activity ratios were measured on a ThermoFisher Neptune Plus multi-collector inductively-coupled plasma mass spectrometer at the Research School of Earth Sciences, Australian National University. Mass bias and SEM-Faraday cups yield were
corrected by standard bracketing using synthetic standard CRM U010 for U and synthetic standard OU Th’U’ for Th. The accuracy of analyses was evaluated by measuring CRM U005A for U and UCSC Th’A’ for Th. Accuracy of sample dissolution, chromatography and analysis was assessed using gravimetric standard QLO-1 (U.S. Geological Survey), which is in secular equilibrium. The U and Th concentrations were within error of recommended values (Abbey and Canada, 1983; Flanagan and Flanagan, 1976; Govindaraju, 1994). The (\(^{234}\text{U}/^{238}\text{U}\)) and (\(^{230}\text{Th}/^{238}\text{U}\)) activity ratios were within 0.17 and 2.3% of secular equilibrium, respectively (Table 4.5). Total procedure blanks were generally <297 and <140 pg for U and Th, respectively, and represented <0.09 and <0.05% of the average mass of U and Th in samples. A replicate of one bulk and one quartz samples were used to assess the external analytical uncertainty. Replicate analysis of leached samples was not performed and we used instead the external analytical uncertainty of the bulk material.

4.3.4 Mass-transfer coefficient

Mass-transfer coefficients are used to quantify gains and losses of elements in the regolith relative to the parent material (e.g. Nesbitt, 1979). This information is useful to understand the evolution and mobilization of elements in a weathering profile. To calculate the mass-transfer coefficient an immobile element needs to be identified and the elements of interest are normalized to it.

Two reasons suggest that titanium (Ti) is the least mobile element analysed in bulk and leached regolith. Firstly, in the literature it has been widely accepted that Ti is not significantly mobilized during weathering (Nesbitt, 1979; Pelt et al., 2008; Stiles et al., 2003). Secondly, in the bulk and leached regolith, Ti concentrations remain similar with varying depths (Table 4.3). In contrast, the concentrations of the other major elements and Zr – commonly considered an immobile element – show variations throughout the weathering profile, indicating losses and gains of these elements during pedogenesis.

For bulk and leached samples, the mass-transfer coefficient for element X (\(\tau_{\text{Ti}, X}\) in %) is calculated using the equation proposed by Nesbitt (1979) and later modified by (Anderson et al. (2002):
\[
\tau_{\text{Ti}, X} (\%) = \left( \frac{(X/\text{TiO}_2)_{\text{sample}}}{(X/\text{TiO}_2)_{\text{bulk bedrock}}} - 1 \right) \times 100
\]

(1)

The resulting values quantify losses and gains of an element X by a regolith sample relative to the bulk bedrock. Positive values indicate gains of element, whereas negative values designate losses.

We were unable to define an immobile element for quartz grains; for this reason, we used elemental concentrations.

### 4.4 Results

#### 4.4.1 Bulk samples

The mineralogical data of the bulk regolith show that the E horizon is dominated by quartz (96-96 wt %), while minor amount of clays (2-3 wt. %) and K-feldspars are present (Table 4.2). Deeper in the B horizon, the concentration of clays sharply increases (21-22 wt. %) and quartz decreases (67-68 wt. %). The mass-transfer coefficients for bulk regolith show that the E horizon is depleted in Mg, Al, K relative to the bedrock, whereas Fe has been lost in the upper and gained in the lower part of the horizon (Figure 4.1). Loss on Ignition values are relatively high in the upper E horizon and decrease sharply in the lower part of this horizon (Figure 4.2). In contrast, the B horizon shows a gain of Mg, Al, K and Fe relative to the E horizon and bedrock. In the upper B horizon, LOI values are the highest measured in the regolith profile and decrease in the lower part of the horizon.

<table>
<thead>
<tr>
<th>Depth (m) / horizon</th>
<th>Quartz</th>
<th>K-feldspar</th>
<th>Plagioclase</th>
<th>Clays</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD2 0.2 / E</td>
<td>94</td>
<td>4</td>
<td></td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>STD4 0.4 / E</td>
<td>96</td>
<td>2</td>
<td></td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>STD10 1.3 / B</td>
<td>68</td>
<td>11</td>
<td></td>
<td>21</td>
<td>100</td>
</tr>
<tr>
<td>STD12 1.8 / B</td>
<td>67</td>
<td>5</td>
<td>6</td>
<td>22</td>
<td>100</td>
</tr>
<tr>
<td>STD Bedrock</td>
<td>94</td>
<td>4</td>
<td>2</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>
Clays are illite, chlorite and kaolinite.

Figure 4.1. Mass-transfer coefficients for Mg (a), Al (b), K (c) and Fe (d) as a function of depth. The dashed lines indicate the boundary between the E and B horizons. The error bars are propagated external analytical uncertainties (RSE). In these diagrams and in the following, when error bars are not shown, they are within symbol size; furthermore, the bedrock depth is estimated between 3 and 10 m (TERN).
In the bulk regolith, mass-transfer coefficients show U depletion only in the upper E horizon (Figure 4.3). Uranium enrichment increases in the lower E and upper B horizon, whereas a lesser enrichment of U is displayed in the lower B horizon. Thorium shows a similar trend: it is depleted in the E horizon and increasingly enriched in the B (Figure 4.3). The $^{234}\text{U}/^{238}\text{U}$ activity ratios are lower than one in the E horizon and show analogous values. In the B horizon, $^{234}\text{U}/^{238}\text{U}$ are very variable, showing a values near unity in the upper part of the horizon and less than 1 in the lower part (Figure 4.3). In the regolith, $^{230}\text{Th}/^{238}\text{U}$ are below 1; the lower values are observed in the upper B horizon and in the lower E (Figure 4.3).

Figure 4.2. Loss on Ignition (LOI) measured at 550°C for bulk and leached samples (in wt %) versus regolith depth. The dashed line indicates the boundary between E and B horizons. The error bars are external analytical uncertainties (RSE).
The bedrock mineralogy is dominated by quartz (94 wt. %) and minor amount of K-feldspars and plagioclase (Table 4.2). The concentrations of major elements, U and Th, shown in Table 4.3 and 5, are comparable to the ones commonly found in the literature for sandstones (Turekian and Wedepohl, 1961). The bulk bedrock shows $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U activity ratios greater than unity (Table 4.5).

### 4.4.2 Leached samples

Sequential extraction resulted in a loss of all major elements in the B horizon and, to a lesser extent, in the E horizon (Figure 4.1). A loss of organic matter following sequential extraction is also evident from the lower LOI values found in leached samples (Figure
The leached samples are generally depleted in U compared to the bulk, except for the leached, upper E horizon which is enriched in this element (Figure 4.3). While the lower B horizon shows a relatively high $\tau_{\text{Ti, U}}$ value, the other regolith samples show a quasi-constant U enrichment throughout the profile. This contrasts with the very variable $\tau_{\text{Ti, U}}$ values observed in bulk regolith. Sequential extraction resulted in higher $\tau_{\text{Ti, Th}}$ values in the E horizon and in lower values in the B horizon when compared to the bulk samples (Figure 4.3).

The ($^{234}\text{U}/^{238}\text{U}$) activity ratios show little changes following sequential extraction (Figure 4.3), except for the upper B horizon where depletion of $^{234}\text{U}$ relative to $^{238}\text{U}$ is observed. The ($^{230}\text{Th}/^{238}\text{U}$) of leached regolith display similar values to bulk samples, except for the bulk samples that show extremely low ($^{230}\text{Th}/^{238}\text{U}$); in those cases the ($^{230}\text{Th}/^{238}\text{U}$) of the respective leached samples is significantly higher than in the bulk (Figure 4.3).

In the leached bedrock, the mass-transfer coefficients show no variation in Mg, Al, K and U when compared to the bulk bedrock, whereas they display significant loss of Fe and Th (Figures 4.1 and 4.3). Following sequential extraction the ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) remain unchanged relative to the bulk samples (Figure 4.3).

### 4.4.3 Quartz separates

Quartz separated from the regolith shows lower concentrations of Mg, Fe, Ti and K compared to the quartz separated from the bedrock (Figure 4.4). These concentrations remain relatively constant throughout the weathering profile. The only exceptions are the K concentrations observed in the E horizon, which are greater than those found in the rest of the profile.
The U and Th concentration in quartz separates decrease with decreasing depth (Figure 4.5). In the bedrock, quartz separates are in secular equilibrium for the $^{234}$U-$^{238}$U system but show a depletion of $^{230}$Th over $^{238}$U (Figure 4.3). The ($^{234}$U/$^{238}$U) show variation with depth similar to those observed for the bulk and leached samples (Figure 4.3): ($^{234}$U/$^{238}$U) decrease from the bedrock to the B horizon and then increase toward unity with decreasing depth. Compared to bulk and leached samples, quartz separates generally show lower ($^{230}$Th/$^{238}$U) activity ratios, and values overall decrease with depth.

Figure 4.4. Concentrations of Mg, K, Fe and Ti (in ppm) in quartz separate versus regolith depth. The error bars are external analytical uncertainties (RSE).
4.5 Discussion

4.5.1 Bulk samples

The E horizon is largely dominated by quartz, while little amounts of feldspar and clays are present (Table 4.2). In contrast, the B horizon displays a high content of clay minerals. This suggests that phases, such as clays, and elements (e.g. Fe, Al) could be eluviated from the E horizon and illuviated into the B horizon. The relatively high LOI values observed in the bulk, B horizon, which are used as a proxy for organic matter content, suggest that also organic matter has been eluviated/translocated from the E horizon, where it is produced (Figure 4.2; Donkin, 1991; Heiri et al., 2001). These processes are characteristic of podzols. Note that in the B horizon the high LOI values may be partially
due to clay dehydration, a reaction that may occur during this procedure (Heiri et al., 2001).

The mass-transfer coefficients for major elements, U and Th indicate a general depletion of Ma, Al, K, Fe, U and Th in the E horizon accompanied by an enrichment in these elements in the B horizon (Figures 4.1 and 4.3). This reflects the podzolisation process, in which major elements, and possibly U and Th are eluviated from the E horizon and illuviation in the B horizon (Crançon et al., 2010; Crançon and Van der Lee, 2003; Lundström et al., 2000; Rihs et al., 2011). It is also possible that clay minerals containing the same elements are translocated from the E into the B horizon; this is supported by the mineralogy data, which show high clay content in the B horizon. Iron and uranium behave slightly differently compared to the other elements analysed; only the upper E horizon is depleted in these elements, while the lower E horizon is enriched. This suggests that Fe and U are removed predominantly from the upper horizon and are precipitated in the lower E horizon. Similarly, to the major elements and Th, Fe and U continue to be stored in the B horizon.

In general, the upper B horizon is more enriched in major elements and U compared to the lower B horizon, except for K and Th which show the opposite trend (Figures 4.1 and 4.3). This suggests that most illuviation/clay translocation is concentrated in the upper B horizon. In this horizon, the presence of Fe-oxides, clays and organic matter may play together and result in large immobilization of U. The affinity of U for these phases is well known: U can be adsorbed onto Fe-oxides, clays and organic matter, and/or co-precipitate from the water solution with Fe-oxides and organic matter (Abdelouas et al., 1998; Ames et al., 1983a; Chabaux et al., 2003; Cowart and Burnett, 1994; Duff et al., 2002; Hsi and Langmuir, 1985; Murphy and Shock, 1999; Syed, 1999). In contrast, Th is transported deeper in the profile; the maximum gain of Th coincides with high Al gains and smaller accumulation of Fe and organic matter. The affinity of Th with clays and, to a lesser extent, Fe-oxide and organic matter may explain this observation (Chabaux et al., 2003; Chen and Wang, 2007; Guo et al., 2005; Schulz, 1965; Syed, 1999).

The \( \frac{^{234}U}{^{238}U} \) activity ratios and the \( \tau_{\text{Th},U} \) values of bulk samples show similar pattern of variation with depth (Figure 4.3). The upper E horizon shows \( \frac{^{234}U}{^{238}U} < 1, \)
suggesting that here the dominant process controlling this activity ratio is the removal of U enriched in $^{234}$U relative to $^{238}$U, likely by water solution (Andersen et al., 2009a; Chabaux et al., 2003). In the lower E and upper B horizons, where U is illuviated, the ($^{234}$U/$^{238}$U) increase relative to the upper E horizon. This suggests that the $^{234}$U - $^{238}$U system is dominated by gain of U enriched in $^{234}$U relative to $^{238}$U and supports the hypothesis that the U eluviated from the upper E horizon is transported by solution and illuviated in the lower E and B horizons. In the lower B horizon, the mass-transfer coefficient shows that little U is illuviated accompanied by low ($^{234}$U/$^{238}$U). This suggests that, although little illuviation of U form the upper horizon, the major process controlling ($^{234}$U/$^{238}$U) is removal of U enriched in $^{234}$U relative to $^{238}$U, possibly due to dissolution of bedrock-derived phases during pedogenesis.

The ($^{230}$Th/$^{238}$U) activity ratios lower than one through the regolith profile indicate an excess of $^{238}$U relative to $^{230}$Th (Figure 4.3). It is possible that in this profile $^{230}$Th is more mobile than $^{238}$U. A possible explanation is that, similarly to $^{234}$U, $^{230}$Th is preferentially mobilized relative to $^{238}$U during weathering processes. In a mineral grain, $^{230}$Th is produced by alpha-decay and the energy released during the reaction could directly eject $^{230}$Th out the host-grain or displace it inside the grain crystal lattice, creating a damaged site (recoil track; Kigoshi, 1971). As $^{230}$Th is located in damaged sites, it can also be easily leached out during weathering processes. Once leached out, $^{230}$Th is expected to be re-adsorbed because of it low mobility; however, in the presence of organic and, to a lesser extent, inorganic complexes Th mobility can be significantly enhanced (Dosseto, 2015; Langmuir and Herman, 1980).

The U-series isotopic analyses show that the bedrock is not in secular equilibrium (Table 4.5). This suggests that the bedrock has experienced weathering during the last Myr; this could be explained by the fact that the sample was collected from an outcrop and could have been exposed to weathering. The bedrock shows enrichment in $^{230}$Th and $^{234}$U relative to $^{238}$U. Enrichment in $^{230}$Th relative to $^{238}$U could be explained by U loss, whereas enrichment in $^{234}$U relative to $^{238}$U cannot be explained by the expected nuclide mobility. In the bedrock, the ($^{234}$U/$^{238}$U) activity ratio greater than unity could be produced by i) preferential mobilization of $^{238}$U than $^{234}$U and/or ii) $^{234}$U addition occurring during
weathering. Activity ratios greater than one were reported by Chabaux et al. (2013) for a corestone collected from a regolith; to explain this activity ratio they hypothesised simultaneous loss of $^{238}\text{U}$ and gain of $^{234}\text{U}$ occurring during incipient weathering, assuming that Th remains immobile. The same hypothesis could explain the isotopic composition observed in our bedrock.

### 4.5.2 Sequential extraction

In the bulk material, we observe a general trend in which major elements, organic matter, U and Th are eluviated from the E horizon and illuviated in the B horizon. This process is likely to form illuviated, solution-derived phases and organic aggregates. In addition, we hypothesise that clay minerals are translocated from the upper to the lower part of the profile. Here, we compare the information inferred from mineralogical and major elements analyses in bulk and leached samples to test whether sequential extraction removes illuviated material.

Following sequential extraction of the E horizon, mass-transfer coefficients display no significant loss or gain of Mg, Al, K and Fe, suggesting that sequential extraction does not remove phases containing these elements (Figure 4.1). This indicates that in the E horizon the phases targeted by sequential extraction (Fe-oxides, carbonates and organic matter) are not present; this could be the result of eluviation, which may have removed labile phases from this horizon, leaving only resistant minerals (i.e. quartz). A way to evaluate whether or not sequential extraction removes any phases is to compare the mass of the dry samples before and after treatment. This measurement was not performed in this study; we suggest measuring this mass variation in future experiments involving sequential extraction. In contrast, in the B horizon, sequential extraction results in a loss of Mg, Al, K and Fe (Figure 4.1). However, leached samples still show an enrichment of these elements relative to the E horizon and the bedrock. This suggests that, in the B horizon, sequential extraction removes only a fraction of the gained Mg, Al, K and Fe, retained in Fe-oxides, carbonates and organic matter, whereas a second fraction remains in the leached sample. This fraction may be retained in clay minerals and/or in other solution-derived phases that are not dissolved by sequential extraction.
The LOI data show that sequential extraction systematically removes organic matter in all horizons (Figure 4.2). If the upper B horizon is not taken into account, the similar LOI values observed for the leached samples (between 0.5 and 1.6 wt %) and the bedrock (1.5 wt %) suggest that sequential extraction effectively removes organic matter from all areas of the profile. The LOI values slightly greater than zero observed in leached samples and bedrock may be produced by clay and metal oxide dehydration and/or removal of volatile salts (Heiri et al., 2001). In the leached, upper B horizon the LOI value is higher than in all the other horizons; this suggests that sequential extraction may not completely remove organic matter.

When comparing the U and Th mass-transfer coefficients for the bulk and leached samples, the E horizon shows both losses and anomalous gains of U and Th (Figure 4.3). Uranium and Th gains are unexpected as sequential extraction is supposed to remove material. An explanation is that U and Th concentrations in the E horizon samples could be heterogeneous and the bulk and leached samples are characterized by different U and Th concentrations. Table 4.5 supports this hypothesis, showing that U (see sample STD 2) and Th (see sample STD 4) concentrations in leached and bulk samples are substantially different. Alternatively, it is possible that, in the E horizon, sequential extraction results in greater mobilization of Ti relative to U and Th. In this case, $\tau_{\text{i, U}}$ and $\tau_{\text{i, Th}}$ in leached samples would be greater than in bulk samples. Note that if this is the case, losses of other elements (i.e. U, Th, Mg, Al, K and Fe) from the E horizon following sequential extraction would be underestimated.

In the E horizon, the variation in $\tau_{\text{i, U}}$ and $\tau_{\text{i, Th}}$ in leached samples relative to bulk are accompanied by unchanged $^{(234}\text{U}/^{238}\text{U})$ and $^{(230}\text{Th}/^{238}\text{U})$ activity ratios, except for the lower sample where large $^{238}\text{U}$ enrichments disappear after sequential extraction (Figure 4.3). The unchanged activity ratios indicate that sequential extraction does not result in the fractionation of the $^{234}\text{U} - ^{238}\text{U}$ and $^{230}\text{Th} - ^{238}\text{U}$ systems. This can be explained by two hypotheses: i) U and Th removed have the same $^{(234}\text{U}/^{238}\text{U})$ and $^{(230}\text{Th}/^{238}\text{U})$ of the bulk samples; or ii) sequential extraction does not remove a sufficient amount of U and Th to produce isotopic fractionation. The first hypothesis is unlikely, as our data indicate that sequential extraction removes only organic matter from the bulk E horizon, which is
expected to show \((^{234}\text{U}/^{238}\text{U}) > 1\) and \((^{230}\text{Th}/^{238}\text{U}) < 1\). Removal of organic matter is expected to decrease \((^{234}\text{U}/^{238}\text{U})\) and increase \((^{230}\text{Th}/^{238}\text{U})\) in leached samples, which is not the case. The second hypothesis is more likely, as major elements analyses indicate that sequential extraction does not significantly remove mineral phases (e.g. Fe-oxides, carbonates) from the E horizon. The increase in \((^{230}\text{Th}/^{238}\text{U})\) in the lower E horizon following sequential extraction suggests removal of phases enriched in \(^{238}\text{U}\) relative to \(^{230}\text{Th}\). Such an isotopic composition is expected for solution-derived phases and/or organic matter. It is possible that sequential extraction removes organic matter containing a little pool of U and Th that is able to affect the \(^{230}\text{Th} - ^{238}\text{U}\) system but not the \(^{234}\text{U} - ^{238}\text{U}\). In general, sequential extraction does not affect the U-series isotope composition of the E horizon, except for the lower sample where removal of organic matter may result in greater \((^{230}\text{Th}/^{238}\text{U})\) when compared to the bulk sample.

Compared to bulk samples, the leached upper B horizon shows a loss of U and Th accompanied by \((^{234}\text{U}/^{238}\text{U})\) decrease and \((^{230}\text{Th}/^{238}\text{U})\) increase (Figure 4.3). These observations suggest that sequential extraction removes Fe-oxides, carbonates and organic matter containing a pool of U and Th enriched in \(^{234}\text{U}\) relative to \(^{238}\text{U}\), and enriched in \(^{238}\text{U}\) relative to \(^{230}\text{Th}\). The lower B horizon displays unchanged \(\tau_{\text{ti, U}}\), \((^{234}\text{U}/^{238}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\), but lower \(\tau_{\text{ti, Th}}\), when compared to the bulk. This indicates that the phases removed by sequential extraction do not contain significant amount of U and that the pool of Th removed contains an amount of \(^{230}\text{Th}\) insufficient to affect the \((^{230}\text{Th}/^{238}\text{U})\).

In general, the leached regolith shows relatively similar \(\tau_{\text{ti, U}}\) and \(\tau_{\text{ti, Th}}\) values (greater than zero) in most horizons (Figure 4.3), except for the lower B and upper E horizons where greater enrichment of U and depletion of Th are observed, respectively. Similar mass-transfer coefficients indicate the presence of a pool of U and Th in excess relative to the one derived from the bedrock and that could have been introduced by dust deposition and/or groundwater, and successively distributed throughout the profile. As this pool is not removed by sequential extraction, it could be retained in clay minerals.

In the bedrock, leached and bulk samples show no variation in Mg, Al, K, U, \((^{234}\text{U}/^{238}\text{U})\) and \((^{230}\text{Th}/^{238}\text{U})\), whereas loss of Th and Fe are observed (Figures 4.1 and 4.3). This
suggests that sequential extraction i) does not remove most of primary minerals as major elements remain nearly unchanged, ii) it does not mobilize U, iii) it removes a pool of Fe and Th, which contain a little amount of $^{230}$Th. It is possible that the pool of Fe removed is contained in Fe-oxide present in the bedrock. They could have been formed during weathering, as this sample was collected from an outcrop. Mobilization of Th during early weathering of rocks was observed by Pliler and Adams (1962) and Tilton et al. (1955) and can explain the loss of Th.

Overall, sequential extraction effectively removes U-series isotopes that have been eluviated/illuviated throughout the profile and that are contained in Fe-oxides, carbonates and organic matter. Hence, we recommend this treatment for this type of regolith profiles.

4.5.3 Quartz

In the bedrock, ($^{234}$U/$^{238}$U) activity ratio of quartz is in secular equilibrium, whereas the ($^{230}$Th/$^{238}$U) indicates depletion in $^{230}$Th relative to $^{238}$U. This could be explained by loss of $^{230}$Th, but not U, during incipient weathering of quartz. Thorium-230 may be mobilized by recoil and/or preferential leaching from recoil tracks. Interestingly, the bulk bedrock shows enrichment in $^{230}$Th and $^{234}$U relative to $^{238}$U, suggesting that other minerals in the bedrock (i.e. K-feldspar and plagioclase) may fractionate U-series isotopes differently.

In quartz separates, concentrations of Mg, K, Ti and Fe show dramatic decreases during the transition between the bedrock and the deeper B horizon, and then they remain nearly unchanged throughout the rest of the profile (Figure 4.4). This suggests that quartz contains a pool of these elements that is removed during incipient weathering. Once this pool is exhausted, quartz does not lose significant amount of Mg, K, Ti and Fe, suggesting that it does not significantly decompose during pedogenesis. In the E horizon, K concentrations are greater than the rest of the profile, suggesting gain of this element. The reason for this increase in K concentration is unclear; adsorption of K from water solution onto quartz could explain this observation. For instance, Pal et al. (1999) observed K adsorption occurring onto quartz-rich soils from Australia.

The concentrations of U and Th in quartz dramatically drop in the transition between the bedrock and the lower B horizon, accompanied by a general decrease in ($^{234}$U/$^{238}$U) and
This indicates that a pool of U and Th, enriched in $^{234}$U and $^{230}$Th relative to $^{238}$U, is removed during the conversion of bedrock into the lower B horizon. Loss of U and Th during incipient weathering of rocks has already been observed in other studies; for instance, fast loss of U during incipient weathering of bedrock was observed by Pliler and Adams (1962) and Tilton et al. (1955). These authors hypothesised that a labile fraction of U in unweathered rock could be mobilized during incipient weathering. The decrease in $(^{234}$U/$^{238}$U) occurring during the transition bedrock – B horizon reflects the greater mobility of $^{234}$U relative to $^{238}$U. The decrease in $(^{230}$Th/$^{238}$U) indicates that $^{230}$Th is preferentially mobilized from quartz than $^{238}$U; this could be explained by recoil and/or preferential leaching from recoil-tracks (Kigoshi, 1971). A similar process was observed in bulk bedrocks in the study reported in Chapter 3 and by Dosseto et al. (2012). Hence, during incipient weathering of the bedrock, quartz loses significant amount of U and Th.

In the regolith, quartz separates show an overall decrease in U and Th concentrations with decreasing depth, whereas $(^{234}$U/$^{238}$U) increase and $(^{230}$Th/$^{238}$U) are variable. This suggests that during pedogenesis quartz grains lose U and Th, and $^{238}$U is preferentially mobilized relative to $^{234}$U. This is in contrast with the observations made above; during the conversion of the bedrock into the B horizon we hypothesised that quartz preferentially loses $^{234}$U relative to $^{238}$U. An explanation is provided by Andersen et al. (2009a) who performed a 1100-hour leaching experiment of a crushed rock. The authors found that during the first stage of leaching (~500 hr) $^{234}$U is preferentially removed in solution relative to $^{238}$U. In this case, the residual rock will show the expected $(^{234}$U/$^{238}$U) <1. Nevertheless, during the rest of the experiment the pool of easy leachable $^{234}$U extinguished and, in turn, $^{238}$U was preferentially dissolved relative to $^{234}$U. In such a case, the solid residue is expected to show increasing $(^{234}$U/$^{238}$U). In our study, the isotopic composition of quartz in the lower B horizon reflects the processes hypothesised by Andersen et al. (2009a) during the first stage of leaching; a pool of easy leachable $^{234}$U is lost during incipient weathering. Because quartz is not rich in U and Th, it is likely that these elements are located in impurities and/or inclusions within quartz grains. In quartz of the B horizon, this pool could be exhausted and throughout the rest of the regolith $^{238}$U is preferentially lost relative to $^{234}$U, resulting in a general increase in $(^{234}$U/$^{238}$U) with decreasing depth.
In addition, the increase in $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ shown in the upper B horizon relative to the lower B horizon may be amplified by the effect of time. Following the initial loss of U and Th during the conversion of the bedrock into saprolite and consequent decrease in $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$, quartz separates are slightly weathered in this part of the regolith, as displayed by little variations in elemental composition (Figures 4.4 and 4.5). Because of this, it is possible that in the B horizon these two activity ratios increase toward secular equilibrium.

In the regolith, quartz is more depleted in $^{230}\text{Th}$ relative to $^{238}\text{U}$ when compared to bulk and leached samples. Greater mobility of $^{230}\text{Th}$ relative to $^{238}\text{U}$ was previously explained by radioactive decay and consequent alpha-recoil of $^{230}\text{Th}$ in mineral lattice (see section 4.1). It is possible that $^{230}\text{Th}$ in quartz is retained in damaged sites of the crystal lattice and/or in impurities/inclusions, and is preferentially lost with respect to $^{238}\text{U}$ during weathering processes.

Overall, the U-series isotopic composition of quartz separates in the regolith is dominated by U and Th loss, possibly due to mineral dissolution processes. Because quartz is not rich in U and Th, it is likely that these elements are located in impurities and/or inclusions within quartz grains. Our results do not indicate any influence of secondary phases and/or organic matter on the isotopic composition of quartz; this suggests that this mineral could be used to study the fractionation of U-series isotopes during regolith formation and, potentially, to estimate regolith production rates (quartz residence time in regolith).

4.6 Conclusions

The aim of this article is to define a method to isolate bedrock-derived phases from a sandstone regolith profile and study their U-series isotopic evolution with depth. To do this, solution-derived minerals and organic matter need to be removed. For this purpose, sequential extraction and separation of quartz from the regolith are tested. The definition of a method to isolate bedrock-derived phases from regolith and their isotopic composition has the potential of improving the current method to estimate regolith production rates using U-series isotopes (Dosseto, 2015; Dosseto et al., 2008b; Suresh et al., 2014).
The studied weathering profile is a podzol. In bulk samples, mass-transfer coefficients for major elements, U and Th, together with U-series isotopic and XRD analyses, indicate that significant amount of Mg, Al, Fe, K, U, Th and clays have been eluviated from the E horizon and immobilized into the B horizon. We aim at removing eluviated phases from the bulk samples.

Sequential extraction of the E horizon suggests that only organic matter is removed by this treatment, when compared to the bulk samples. This indicates that the other phases targeted by sequential extraction are not present in this horizon, possibly because they have been eluviated during pedogenesis. In the E horizon, sequential extraction does not remove significant amount of U and Th, and does not affect the $^{234}\text{U} - ^{238}\text{U}$ system; however, we observe an increase in $(^{230}\text{Th}/^{238}\text{U})$ following sequential extraction, suggesting removal of phases enriched in $^{238}\text{U}$ relative to $^{230}\text{Th}$, likely organic matter. In the B horizon, sequential extraction seems to remove Fe-oxides, carbonates and organic matter. This affects only the isotopic composition of the upper B horizon, where the removal of U and Th is accompanied by a decrease in $(^{234}\text{U}/^{238}\text{U})$ and an increase in $(^{230}\text{Th}/^{238}\text{U})$. In contrast, in the lower B horizon only a pool of Th is removed, whereas $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ remain unchanged relative to the bulk samples. Overall, sequential extraction effectively removes Fe-oxides, carbonates and organic matter containing U-series isotopes that have been eluviated/illuviated throughout the regolith. We recommend sequential extraction for U-series analyses of similar regolith profiles (i.e. podzol).

Quartz separates show that a pool of major elements, U and Th is released during the transition between the bedrock and the lower B horizon. This is accompanied by a decrease in $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ to values lower than unity. This suggests a large loss of U-series isotopes occurring during incipient weathering, with $^{234}\text{U}$ and $^{230}\text{Th}$ preferentially mobilized than $^{238}\text{U}$. The U-series isotopic composition of quartz throughout the regolith suggests that during pedogenesis this mineral loses U and Th enriched in $^{238}\text{U}$ relative to $^{234}\text{U}$, whereas no evidences suggest gain of U and/or Th. Quartz records the fractionation of U-series isotopes during regolith formation and could
be a candidate material to estimate regolith production rates (quartz residence time in regolith).
### Table 4.3. Major element compositions for bulk and leached samples (in wt %).

<table>
<thead>
<tr>
<th>Sample ID / horizon</th>
<th>Na2O</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>P2O5</th>
<th>SO3</th>
<th>K2O</th>
<th>CaO</th>
<th>TiO2</th>
<th>MnO</th>
<th>Fe2O3</th>
<th>LOI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STD2 / E</td>
<td>&lt; 0.02</td>
<td>0.0092</td>
<td>1.16</td>
<td>93.1</td>
<td>&lt; 0.01</td>
<td>0.042</td>
<td>0.117</td>
<td>0.064</td>
<td>0.37</td>
<td>0.01</td>
<td>0.420</td>
<td>3.71</td>
<td>99</td>
</tr>
<tr>
<td>STD4 / E</td>
<td>&lt; 0.02</td>
<td>0.010</td>
<td>1.32</td>
<td>95.4</td>
<td>&lt; 0.01</td>
<td>0.017</td>
<td>0.111</td>
<td>0.040</td>
<td>0.35</td>
<td>0.01</td>
<td>0.981</td>
<td>1.26</td>
<td>99</td>
</tr>
<tr>
<td>STD10 / B</td>
<td>&lt; 0.02</td>
<td>0.18</td>
<td>10.0</td>
<td>80.6</td>
<td>0.011</td>
<td>0.014</td>
<td>0.842</td>
<td>0.020</td>
<td>0.39</td>
<td>0.005</td>
<td>2.43</td>
<td>5.08</td>
<td>100</td>
</tr>
<tr>
<td>STD12 / B</td>
<td>&lt; 0.02</td>
<td>0.12</td>
<td>7.52</td>
<td>87.5</td>
<td>0.018</td>
<td>0.014</td>
<td>1.20</td>
<td>0.022</td>
<td>0.34</td>
<td>0.004</td>
<td>0.587</td>
<td>2.75</td>
<td>100</td>
</tr>
<tr>
<td>STD Bedrock rep.1</td>
<td>&lt; 0.02</td>
<td>0.024</td>
<td>3.21</td>
<td>93.3</td>
<td>0.013</td>
<td>0.0058</td>
<td>0.376</td>
<td>0.059</td>
<td>0.49</td>
<td>0.01</td>
<td>0.637</td>
<td>1.85</td>
<td>100</td>
</tr>
<tr>
<td>STD Bedrock rep.2</td>
<td>&lt; 0.02</td>
<td>0.024</td>
<td>3.16</td>
<td>93.4</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>0.387</td>
<td>0.056</td>
<td>0.50</td>
<td>0.01</td>
<td>0.611</td>
<td>1.11</td>
<td>99</td>
</tr>
</tbody>
</table>

| **Leached**         |      |      |       |       |      |      |      |      |      |      |       |     |       |
| STD2 / E            | < 0.02 | 0.0065 | 0.792 | 96.2  | < 0.01 | 0.0068 | 0.0893 | 0.35  | 0.29 | 0.004 | 0.258 | 1.28 | 99    |
| STD4 / E            | < 0.02 | 0.0060 | 0.719 | 96.9  | 0.037  | 0.016  | 0.0752 | 0.26  | 0.23 | 0.004 | 0.587 | 0.554 | 99    |
| STD10 / B           | < 0.02 | 0.047  | 5.95  | 87.7  | 0.0029 | 0.011  | 0.606  | 0.33  | 0.29 | 0.004 | 1.40  | 2.96  | 99    |
| STD12 / B           | < 0.02 | 0.029  | 3.92  | 91.8  | 0.0033 | 0.011  | 0.680  | 0.82  | 0.22 | 0.003 | 0.228 | 1.64  | 99    |
| STD Bedrock         | < 0.02 | 0.025  | 3.29  | 93.1  | < 0.01 | 0.0025 | 0.324  | 0.59  | 0.47 | 0.003 | 0.129 | 1.52  | 99    |

| **Estimated external relative analytical uncertainties (RSE)** | - | 0.0 | 0.56 | 0.038 | - | - | 1.0 | 1.8 | 0.71 | 0.0 | 1.5 | 18 |

The reported external relative analytical uncertainties (RSE) were calculated as the standard error of the average of duplicates measurements for two bulk bedrocks.
Table 4.4. Trace element concentrations in quartz separates (in ppm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth / horizon</th>
<th>Na [ppm]</th>
<th>RSD</th>
<th>Mg [ppm]</th>
<th>RSD</th>
<th>Ti [ppm]</th>
<th>RSD</th>
<th>Fe [ppm]</th>
<th>RSD</th>
<th>K [ppm]</th>
<th>RSD</th>
<th>Zr [ppm]</th>
<th>RSD</th>
<th>Relative external analytical uncertainties (RSE; %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD2</td>
<td>0.15 / E</td>
<td>24.2</td>
<td>3.9</td>
<td>29.5</td>
<td>2.3</td>
<td>103</td>
<td>2.2</td>
<td>185</td>
<td>0.82</td>
<td>588</td>
<td>41</td>
<td>0.44</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>STD4</td>
<td>0.35 / E</td>
<td>15.8</td>
<td>7.9</td>
<td>31.2</td>
<td>3</td>
<td>107</td>
<td>1.5</td>
<td>192</td>
<td>2.4</td>
<td>949</td>
<td>68</td>
<td>0.43</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>STD10</td>
<td>1.3 / B</td>
<td>44.8</td>
<td>3.5</td>
<td>85.7</td>
<td>0.75</td>
<td>186</td>
<td>1.3</td>
<td>348</td>
<td>3.2</td>
<td>46</td>
<td>4.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>STD12 rep.1</td>
<td>1.8 / B</td>
<td>21.9</td>
<td>4.4</td>
<td>43.8</td>
<td>1.8</td>
<td>120</td>
<td>1.1</td>
<td>113</td>
<td>1.5</td>
<td>76.4</td>
<td>6.2</td>
<td>0.47</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>STD12 rep.2</td>
<td>1.8 / B</td>
<td>45.1</td>
<td>6.2</td>
<td>50.5</td>
<td>2</td>
<td>164</td>
<td>2.1</td>
<td>153</td>
<td>2.3</td>
<td>197</td>
<td>8.8</td>
<td>0.98</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>STD Bedrock</td>
<td>2</td>
<td>59.8</td>
<td>2.2</td>
<td>366</td>
<td>1.8</td>
<td>913</td>
<td>1.1</td>
<td>721</td>
<td>2.7</td>
<td>46.2</td>
<td>3</td>
<td>33.7</td>
<td>0.73</td>
<td></td>
</tr>
</tbody>
</table>

The reported external relative analytical uncertainties (RSE; %) were calculated as the standard error of the average of duplicates measurements of sample STD 12.
Table 4.5. U-series isotope compositions of bulk and leached samples, and quartz separates. Reported external relative analytical uncertainties (RSE) were calculated as the standard error of the average of duplicates measurements for on bulk sample, one leached and one quartz separate.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Depth (m) / horizon</th>
<th>Th (ppm)</th>
<th>2SE</th>
<th>U (ppm)</th>
<th>2SE</th>
<th>$^{238}\text{U}/^{235}\text{U}$</th>
<th>2SE</th>
<th>$^{230}\text{Th}/^{238}\text{U}$</th>
<th>2SE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDT2</td>
<td>0.2 / E</td>
<td>2.87</td>
<td>0.002</td>
<td>0.73</td>
<td>0.001</td>
<td>0.945</td>
<td>0.002</td>
<td>0.827</td>
<td>0.004</td>
</tr>
<tr>
<td>SDT4</td>
<td>0.4 / E</td>
<td>3.17</td>
<td>0.003</td>
<td>1.41</td>
<td>0.003</td>
<td>0.958</td>
<td>0.003</td>
<td>0.490</td>
<td>0.002</td>
</tr>
<tr>
<td>SDT10</td>
<td>1.3 / B</td>
<td>8.96</td>
<td>0.01</td>
<td>2.45</td>
<td>0.005</td>
<td>1.011</td>
<td>0.002</td>
<td>0.494</td>
<td>0.003</td>
</tr>
<tr>
<td>SDT12</td>
<td>1.8 / B</td>
<td>9.09</td>
<td>0.01</td>
<td>1.45</td>
<td>0.004</td>
<td>0.878</td>
<td>0.002</td>
<td>0.848</td>
<td>0.006</td>
</tr>
<tr>
<td>STD Bedrock rep.1</td>
<td>2</td>
<td>7.73</td>
<td>0.01</td>
<td>1.44</td>
<td>0.005</td>
<td>1.024</td>
<td>0.002</td>
<td>1.043</td>
<td>0.008</td>
</tr>
<tr>
<td>STD Bedrock rep.2</td>
<td>2</td>
<td>7.73</td>
<td>0.01</td>
<td>1.43</td>
<td>0.004</td>
<td>1.019</td>
<td>0.002</td>
<td>1.024</td>
<td>0.006</td>
</tr>
<tr>
<td><strong>External relative analytical uncertainties (RSE)</strong></td>
<td></td>
<td>±0.00%</td>
<td>±0.38%</td>
<td>±0.17%</td>
<td>±0.66%</td>
<td></td>
<td></td>
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<tr>
<td><strong>Leached</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STD2</td>
<td>0.2 / E</td>
<td>2.56</td>
<td>0.002</td>
<td>0.92</td>
<td>0.002</td>
<td>0.944</td>
<td>0.002</td>
<td>0.879</td>
<td>0.004</td>
</tr>
<tr>
<td>STD4</td>
<td>0.4 / E</td>
<td>3.89</td>
<td>0.004</td>
<td>0.76</td>
<td>0.001</td>
<td>0.951</td>
<td>0.002</td>
<td>0.847</td>
<td>0.005</td>
</tr>
<tr>
<td>STD10 rep.1</td>
<td>1.3 / B</td>
<td>5.82</td>
<td>0.007</td>
<td>0.99</td>
<td>0.002</td>
<td>0.881</td>
<td>0.002</td>
<td>0.968</td>
<td>0.006</td>
</tr>
<tr>
<td>STD10 rep.2</td>
<td>1.3 / B</td>
<td>5.14</td>
<td>0.008</td>
<td>0.90</td>
<td>0.002</td>
<td>0.899</td>
<td>0.002</td>
<td>0.973</td>
<td>0.006</td>
</tr>
<tr>
<td>STD12</td>
<td>1.8 / B</td>
<td>4.34</td>
<td>0.01</td>
<td>0.97</td>
<td>0.003</td>
<td>0.867</td>
<td>0.002</td>
<td>0.839</td>
<td>0.006</td>
</tr>
<tr>
<td>STD BEDROCK</td>
<td>2</td>
<td>6.35</td>
<td>0.01</td>
<td>1.39</td>
<td>0.003</td>
<td>1.030</td>
<td>0.002</td>
<td>1.027</td>
<td>0.006</td>
</tr>
<tr>
<td><strong>External relative analytical uncertainties (RSE)</strong></td>
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<td>±4.4%</td>
<td>±3.5%</td>
<td>±0.72%</td>
<td>±19%</td>
<td></td>
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<tr>
<td><strong>Quartz</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STD2</td>
<td>0.2 / E</td>
<td>0.39</td>
<td>0.0002</td>
<td>0.08</td>
<td>0.0004</td>
<td>0.957</td>
<td>0.012</td>
<td>0.285</td>
<td>0.002</td>
</tr>
<tr>
<td>STD4</td>
<td>0.4 / E</td>
<td>0.40</td>
<td>0.0002</td>
<td>0.07</td>
<td>0.0005</td>
<td>0.912</td>
<td>0.010</td>
<td>0.134</td>
<td>0.001</td>
</tr>
<tr>
<td>STD10</td>
<td>1.3 / B</td>
<td>1.25</td>
<td>0.001</td>
<td>0.19</td>
<td>0.001</td>
<td>0.931</td>
<td>0.009</td>
<td>0.438</td>
<td>0.005</td>
</tr>
<tr>
<td>STD12 rep.1</td>
<td>1.8 / B</td>
<td>0.92</td>
<td>0.001</td>
<td>0.13</td>
<td>0.001</td>
<td>0.881</td>
<td>0.006</td>
<td>0.159</td>
<td>0.002</td>
</tr>
<tr>
<td>STD12 rep.2</td>
<td>1.8 / B</td>
<td>1.12</td>
<td>0.001</td>
<td>0.14</td>
<td>0.001</td>
<td>0.903</td>
<td>0.008</td>
<td>0.229</td>
<td>0.001</td>
</tr>
<tr>
<td>STD BEDROCK</td>
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<td>3.73</td>
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<td>0.56</td>
<td>0.004</td>
<td>1.000</td>
<td>0.009</td>
<td>0.636</td>
<td>0.007</td>
</tr>
<tr>
<td><strong>External relative analytical uncertainties (RSE)</strong></td>
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<td>±2.7%</td>
<td>±0.9%</td>
<td>±12%</td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Gravimetric standards</strong></td>
<td>QLO-1 average (n=3)</td>
<td>4.81</td>
<td>0.0084</td>
<td>1.84</td>
<td>0.0213</td>
<td>1.002</td>
<td>0.0087</td>
<td>0.977</td>
<td>0.0173</td>
</tr>
</tbody>
</table>
References


5 Conclusions

The U-series isotopes are a geochemical tool to estimate regolith production rates (Hansen and Stout, 1968; Rosholt et al., 1966). Rates of regolith production can be estimated by modelling the isotopic composition of a weathering profile at different depths (Dequincey et al., 2002; Dosseto et al., 2008b). The model reconstructs the evolution of U-series isotopic composition of bulk regolith since the U-series isotopes started fractionating at the bedrock-regolith interface and returns regolith production rates. Three main assumptions are made by the model from which regolith production rates are derived (Dosseto et al., 2008b). First, bedrock-derived phases (i.e. residual primary minerals and clays produced as a result of incongruent dissolution of primary minerals) constantly lose U-series isotopes during pedogenesis due to weathering processes. Second, isotopes are constantly added to regolith by processes such as precipitation of solution-derived phases (i.e. all phases precipitated in regolith from solution) and deposition of organic matter. Finally, the two processes mentioned above operate over similar timescales throughout the profile. Dosseto et al. (2012) identified the third assumption as a model drawback; this could result in inaccurate regolith production rates estimated by the model. A possible solution to this is isolation of bedrock-derived phases from bulk regolith and removal of the influence of solution-derived phases and organic matter on the isotopic composition of bedrock-derived phases. This could result in the elimination of isotopes gained during pedogenesis and in the removal from the model that estimates regolith production rates of: i) the assumption of constant nuclides gain during regolith formation and ii) the assumption that U-series isotopes gain and loss occur at similar timescales. In turn, regolith production rates inferred from bedrock-derived phases could be more accurate than the ones estimated from bulk regolith (Suresh et al., 2014). Here, sequential extraction and mineral separation were explored as methods to isolate bedrock-derived phases.

In light of this, the present thesis defined two research questions:
1. Do sequential extraction and/or mineral separation isolate bedrock-derived phases from bulk regolith and remove the influence of solution-derived phases and organic matter on their U-series isotopic composition?

2. As these experiments have never been performed until now, what can we learn about U-series isotopes fractionation during pedogenesis?

These questions were addressed by comparing isotopic, major elements and mineralogical compositions of i) bulk material, ii) residue of sequential extraction (leached samples) and ii) minerals separates of three weathering profiles developed over basalt, granite and sandstone. In each experimental chapter (Chapters 2, 3 and 4) major findings are summarized. This concluding chapter aims at synthesize the most significant results and address the two research questions. Moreover, its objective is to provide implications and limitations of this research as well as recommendations for future developments. First, in section 5.1 the effects of sequential extraction on the three regolith profiles are discussed. Second, section 5.2 examines the outcomes of mineral separation. Finally, breakthroughs in U-series isotopes fractionation during pedogenesis are synthetised in section 5.3.

5.1 Sequential extraction

Sequential extraction is a chemical method to partition specific phases in soil (i.e. Fe-oxides, carbonates and organic matter; Schultz et al., 1998; Tessier et al., 1979). Here, it was tested as a method to remove specific phases from regolith.

In this thesis, sequential extraction of regolith and bedrock resulted into three different types of responses: i) it removed the expected phases and the U-series isotopes retained within them, ii) it did not remove any phases, and iii) it dissolved bedrock-derived phases in addition to solution-derived and organic matter.

Removal of Fe-oxides, carbonates and organic matter, along with U-series isotopes retained in them, was observed in regolith horizons where precipitation of solution-derived phases and deposition of organic matter had occurred during pedogenesis (Chapter 4). In general, when compared to the bulk samples, the leached ones showed loss of U and Th accompanied by a decrease in $^{234}\text{U}/^{238}\text{U}$ and an increase in $^{230}\text{Th}/^{238}\text{U}$.
activity ratios. The B horizon of the sandstone profile (Chapter 4) is an example; during pedogenesis, this horizon experienced illuviation of solution-derived phases and organic matter containing U-series isotopes. Sequential extraction resulted in loss of U and Th, decrease in $^{234}\text{U}/^{238}\text{U}$ and increase in $^{230}\text{Th}/^{238}\text{U}$; this can be interpreted as removal of solution-derived phases. Similar behaviours were showed by the soil of the basaltic weathering profile (Chapter 2). Overall, in soils with characteristics similar to the sandstone regolith examined in this study, sequential extraction removes solution-derived phases and organic matter from regolith and is recommended.

Sequential extraction did not significantly remove any phase from highly weathered or eluviated horizons. In this condition, regolith has experienced dissolution of bedrock-derived phases and little or no precipitation of solution-derived phases and organic matter. This is the case of the E horizon in the sandstone profile (Chapter 4) where sequential extraction did not affect major elements, U and Th contents, as well as $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios. This suggests that no phases containing these elements were removed from this horizon by sequential extraction. In weathered regolith or in eluviated weathering profiles and/or horizons, sequential extraction has little to no effect.

In other samples, sequential extraction dissolved, labile bedrock-derived phases. This event may occur both in the presence and in the absence of solution-derived and/or organic matter dissolution. For instance, sequential extraction dissolved bedrock-derived clays from the saprolite in the basaltic profile (Chapter 2). In the granitic bedrock, which supposedly did not contain solution-derived phases and/or organic matter, sequential extraction (and etching) removed a pool of U and Th likely retained at grain boundaries and/or in inclusions. In these two examples, sequential extraction altered the U-series isotopic composition of leached samples when compared to the bulk material. Removal of bedrock-derived U-series isotopes resulted in artefactual $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ in leached samples. If these isotopic compositions were used to estimate regolith production rates, the model could have returned inaccurate results. Therefore, sequential extraction is not recommended in conditions where it removes bedrock-derived phases.

The reason why sequential extraction has different effects on the basaltic, granitic and sandstone regolith, as well as within their horizons, lies on the different pedogenic and,
consequently, mineralogical characteristics of the three profiles. On the one hand, sequential extraction removes organic matter, carbonates and Fe-oxides phases when they are present. This is shown in the basaltic soil and in the B horizon of the sandstone regolith, in which these phases are present. In these cases, sequential extraction removes the target phases and, hence it is recommended. On the other hand, sequential extraction has little or no effect on horizons and profiles where labile phases are not present; this is the case of the eluviated E horizon in the sandstone profile. Here, all labile phases, such as organic matter, Fe-oxides and carbonates, had been removed by pedogenic processes before sequential extraction, which has no effect on the samples. In contrast, other cases sequential extraction removes phases that are not supposed to be removed, such as bedrock-derived phases (i.e. clays derived from primary mineral weathering). In this case, sequential extraction result in artefactual isotopic compositions and, therefore, is not recommended; this is shown in the basaltic saprolite.

**Effect of sequential extraction on sample mineralogy**

X-ray Diffraction (XRD) measurements were used to assess the mineralogical composition of the samples. In the literature, these data are often considered semi-quantitative and are used as an estimation of the samples mineralogical composition (Hillier, 2000). The mineralogical variations between bulk and leached samples – therefore the effect of sequential extraction – were interpreted using XRD data in combination with major and trace element concentrations, which are quantitative measurements (Chapters 2, 3 and 4). When mineralogical variations were interpreted more emphasis was given to major and trace element quantitative analyses (e.g. mass-transfer coefficients) when compared to XRD data.

In the basaltic bedrock, sequential extraction dissolves primary minerals; i.e. olivine. In contrast, in the granitic bedrock, sequential extraction shows little effect, whereas in the sandstone only secondary Fe-oxides – formed during weathering (the sample was collected from an outcrop) – may be removed. This confirms that sequential extraction protocols need to be used carefully, as they are able to dissolve labile, primary minerals
such as olivine. This may be due to pH as low as 2 and relatively high temperatures used during this procedure (Möller and Giese, 1997; Oelkers and Gislason, 2001). In terms of U-series analysis applied to regolith profile, dissolution of bedrock-derived phases may result in artefacts in the isotopic composition of bedrocks.

In the saprolites, sequential extraction resulted in the removal of clays from the basaltic profile and Fe-oxides and organic matter from the sandstone. In contrast, the absence of significant variations in mass-transfer coefficients in the granitic saprolite suggests that sequential extraction did not remove any phase from bulk material.

In the basaltic soil, sequential extraction resulted in the removal of solution-derived phases and organic matter, whereas in the granitic soil Al-bearing minerals (e.g. clays) as well as organic matter were removed.

In the profile derived from sandstone, sequential extraction has little effect on the upper E horizon because eluviation processes had already leached secondary phases and labile organic matter. In the B horizon, sequential extraction seems to remove organic matter, carbonates and Fe-oxides.

Altogether, this information confirms the importance to evaluate the effect of sequential extraction on any sample. This thesis provides an example of how to assess the effect of sequential extraction on the mineralogy of bedrock, saprolite and rocks.

**Implications**

Sequential extraction could be a useful pre-treatment to study U-series isotopic composition of regolith profiles, e.g. estimation of regolith production rates. This is because it is able to remove specific solution-derived phases such as Fe-oxides and carbonates, as well as organic matter. However, in some cases sequential extraction is not effective or can produce artefacts in the U-series isotopic composition of leached samples. Considering a weathering profile, it is important to assess whether this treatment is suitable for this profile and for each horizon within the profile. This includes investigating two main issues. First, in bulk regolith, it is necessary to infer the evolution of the
weathering profile in terms of U-series isotopic composition and mineralogy. Evidences of the presence of U-series isotopes originated from solution-derived phases and organic matter need to be sought. This can be done by studying mineralogical, major (and trace) elements and U-series isotopic compositions. The experiments reported in this thesis provide three examples in different geological settings. Although the method used in this thesis could not define with certainty whether or not U-series isotopes in regolith are bedrock-derived, the investigation of mineralogical, major elements and U-series isotope compositions of a profile provided indications on possible isotopes fractionation processes at play during pedogenesis. This information can be used to assess whether or not sequential extraction is necessary for a given weathering profile. For instance, if no U-series isotopes contained in solution-derived phases and/or organic matter are found, sequential extraction is not necessary. In contrast, in a regolith that shows nuclides gain via precipitation of solution-derived phases, sequential extraction is likely to result appropriate. Second, it is necessary to deduce if sequential extraction removes solution-derived phases and organic matter but not bedrock-derived phases. Here, this was done by comparing major elements and U-series isotopic composition of bulk and leached samples; Chapters 2, 3 and 4 provide examples of this approach applied to three weathering profiles. We recommend to apply sequential extraction to regolith only after having assessed i) if solution-derived phases are present and ii) whether the treatment does not affect bedrock-derived isotopic composition.

Limits of the study

This thesis underlined two limitations for the proposed approach. First, it was not possible to clearly determine the mineralogy of bulk regolith and leached samples. This could limit the understanding of bulk samples mineralogy and, most importantly, the identification of phases removed by sequential extraction. X-ray Diffraction (XRD) is a method to determine the mineralogy of samples; here it was employed to estimate bedrock and regolith mineralogy (both bulk and leached samples). However, this method is seldom quantitative but, in the best-case scenario, is commonly regarded as semi-quantitative (Hillier, 2000). Moreover, regolith samples normally contain large amount of clay minerals which further complicate quantitative analyses by XRD; this is due to clays
properties such as variations in composition and variable configuration of clay mineral lattice (Brindley, 1980; Hillier, 2000). In this thesis, mineralogical information was inferred by combining evidence provided by XRD analyses and major elements. In bulk samples, major elements and XRD analyses were used to deduce information such as sample mineralogy and mineralogical evolution with depth of weathering profiles. Moreover, phases removed by sequential extraction were inferred by comparing major elemental composition of bulk and leached samples.

Second, difficulties in identifying phases removed from bulk regolith by sequential extraction could result in incomplete understanding of whether or not U-series isotopes retained in solution-derived phases and/or organic matter are completely removed by the treatment. In this thesis, major element and U-series isotopic compositions of bulk and leached samples were compared altogether to infer if the pool of U and Th removed by sequential extraction was solution-derived and/or retained in organic matter. These inferences were based on nuclides general mobility and on the existing knowledge of U-series isotopes mobilization in the environment (e.g. Andersen et al., 2013; Andersen et al., 2009a; Bourdon et al., 2003; Chabaux et al., 2008; Chabaux et al., 2003; Dequincey et al., 2002; Dosseto, 2015; Dosseto et al., 2008a; Dosseto et al., 2008b; Ma et al., 2010; Rihs et al., 2011; Vigier et al., 2005).

Titanium as least mobile element

In this thesis, Ti has been selected as the least mobile element available in the dataset. Gains and losses of other elements from regolith samples were calculated using Ti as a reference (e.g. calculation of mass transfer coefficients, Chapters 3 and 4). This choice has been done based on i) intercomponental ratio method proposed by Chesworth et al. (1981), ii) observations of the behaviour of elements throughout the weathering profiles (e.g. an immobile element is expected to show increasing concentration with decreasing regolith depth), and iii) previous studies in the literature (e.g. Brimhall et al., 1992; Menozzi et al., 2016; Pelt et al., 2008). Although Ti is normally considered nearly immobile (e.g. Pelt et al., 2008), it is important to understand that any elements can be mobilized to some extent in different environmental conditions (e.g. varying pH, in the presence of organic matter/ligands etc.). In the specific case of this thesis, possible
mobilization of Ti was observed during sequential extraction and etching. For instance, in Chapter 2, a decrease in Ti concentrations occurred during the first hour of etching in the bedrock, one saprolite and two soils, suggesting mobilization of this element. In Chapter 3, soil samples showed anomalous enrichment in Ca following sequential extraction, whereas in Chapter 4, U and Th enrichment was observed in soil following sequential extraction; a possible explanation of these observations is that Ti was mobilized. Note that mobilization of Ti did not occur in all samples but it is rather isolated to few examples.

Overall, Ti behaves as an immobile element, although it is possible that, in some cases, it is mobilized by sequential extraction and/or etching. In the cases in which Ti is mobilized, losses of other elements may result underestimated, whereas gains may be artefact. This reflection suggests that during pedogenesis Ti may not be as immobile as previously thought. A solution, and a suggestion for future studies, is to use different and less mobile elements instead of Ti. For instance, a niobium (Nb) and tantalum (Ta) have been successfully used as immobile elements to study the behaviour of refractory elements in volcanic soils (Kurtz et al., 2000).

Future directions

Future developments should investigate methods to quantitatively define mineralogy of regolith. This will provide a breakthrough to better understand the origin of the pool of U-series isotopes removed by this treatment. This could be addressed by exploring XRD methods and adapt them to study the complex mineralogy of regolith (e.g. Hillier, 2000).

Sequential extraction procedures have been used to remove secondary phases from regolith and sediments. They are assumed to selectively remove phases such as Fe-oxides, carbonates and organic matter (Martin et al., 2015; Suresh et al., 2014; Tessier et al., 1979). Future works should verify that sequential extraction specifically removes target phases without dissolving bedrock-derived phases. This could be done by investigating the evolution of major and trace elements composition in leached samples (solid residue) and leaching solutions at different stages of sequential extraction. Alternatively, similarly to what it was proposed above, the development of XRD methodologies specifically
designed for the analyses of regolith could verify that sequential extraction only removes targeted phases.

### 5.2 Mineral separation

Mineral separation revealed to be a suitable tool to study U-series isotopes fractionation in weathering profiles. In addition, mineral separates showed to be promising materials from which derive regolith production rates. This study displayed that in some instances isotopic composition of mineral separates reflects the evolution of bedrock-derived phases during regolith development. This thesis led to three main outcomes.

First, mineral separation is not suitable for every of regolith and in particular for extremely weathered profiles. For example, in the basaltic profile it was not possible to isolate any bedrock-derive mineral by standard mineral separation methods. The profile was extremely weathered and no recognisable bedrock-derived mineral were present.

Second, some minerals could record loss of U and Th during weathering processes and throughout a weathering profile (i.e. quartz). This implies that the U-series isotopic composition of these minerals is not affected by solution-derived phases and/or organic matter. Quartz separated from the granitic and sandstone profile (Chapters 3 and 4) is an example of this hypothesis. From a geochronological point of view the isotopic composition of these minerals could be modelled to estimate mineral residence time in the regolith.

Third, other minerals are not suitable for studying U-series isotope fractionation in weathering profiles (i.e biotite). This is because their U-series isotopic composition is significantly affected by adsorption of solution-derived pools of U and Th. For instance, in Chapter 3, biotite showed uptake of U and Th accompanied by variations in isotopic composition, which suggested significant adsorption of solution-derived minerals. As the isotopic composition of this mineral was affected by solution-derived minerals, it was not recommended to use it for U-series isotopes and geochronological studies.

*Implications*
Before using mineral separation for studying U-series isotopes in weathering profiles, it is important to assess whether minerals of interest record the isotopic evolution of bedrock-derived phases throughout the profile; i.e. their isotopic composition is not affected by solution-derived phases and/or organic matter. In this thesis, this was done by investigating major element and U-series isotopic evolution of minerals with regolith depth. In general, a mineral that records the isotopic evolution of bedrock-derived phases shows loss of major elements, U and Th with decreasing depth. This should be accompanied by decrease in \((^{234}U/^{238}U)\) activity ratios, as during dissolution of bedrock-derived phases \(^{234}U\) is expected to be preferentially removed than \(^{238}U\). For instance, quartz separated from the sandstone regolith showed these characteristics (Chapter 4). In contrast, a mineral that shows gain of U and/or Th throughout regolith is likely subject to adsorption of solution-derived U-series isotopes. An example is biotite separated from the granitic weathering profile (Chapter 3). Minerals with these characteristics are not recommended for U-series isotopes studies of regolith profiles.

**Future directions**

Bedrock-derived minerals other than quartz and biotite should be considered as possible material from which measure U-series isotope composition and estimate regolith production rates. The ideal mineral candidate should i) be relatively common in regolith, ii) contain a measurable amount of U and Th (ppm), iii) be sufficiently resistant to chemical weathering in order to be present in all horizons of a regolith, iv) be sufficiently labile to fractionate U-series isotopes during weathering and v) be simple to isolate from the rest of regolith components. For instance, a possible candidate is magnetite, as it is a common mineral, contains up to 30 ppm of U and Th, is relatively resistant to weathering and is simple to isolate because of its magnetic properties (Anand and Gilkes, 1984; Harmon and Rosholt, 1982; Matelski and Turk, 1947). In contrast, zircon may not be a suitable candidate: although it contains high concentrations of U and Th, it is very resistant to weathering and may not fractionate U-series isotopes.

**5.3 Breakthrough in U-series isotopes fractionation**

On one hand, most of the existing knowledge on U-series isotopes fractionation at the Earth surface suggests the following *expected* mobility: \(^{234}U > ^{238}U > ^{230}Th\) (Andersen et
al., 2013; Bourdon et al., 2003; Chabaux et al., 2008; Chabaux et al., 2003; Dequincey et al., 2002; Dosseto, 2015; Dosseto et al., 2008a; Dosseto et al., 2008b; Ma et al., 2010; Rihs et al., 2011; Vigier et al., 2005). This mobility has been derived from empirical investigations and reflects the overall fractionation processes occurring at the Earth surface. Based on these hypothesis, residues of weathering (e.g. residual bedrock-derived phases in regolith) are expected to show \((^{234}\text{U} / ^{238}\text{U}) < 1\) and \((^{230}\text{Th} / ^{238}\text{U}) > 1\), whereas solution-derived phases normally show the opposite composition (Dosseto et al., 2008b).

On the other hand, the literature offers several experimental studies that contradict the general mobility of U-series isotopes mentioned above and shows cases where \(^{238}\text{U}\) is more mobile than \(^{234}\text{U}\) and others where \(^{230}\text{Th}\) is more mobile than \(^{238}\text{U}\) (e.g. Andersen et al., 2009a; Essien, 1990; Romer and Rocholl, 2004; Sheng and Kuroda, 1986a; Shirvington, 1983; Tanaka et al., 2015). Although the expected mobility of U-series isotopes was confirmed in several occasions in this thesis, a number of other cases suggested that preferential mobilization of i) \(^{230}\text{Th}\) relative to \(^{238}\text{U}\) and ii) of \(^{238}\text{U}\) relative to \(^{234}\text{U}\) could play a more important role during pedogenesis than previously thought.

Greater mobility of \(^{230}\text{Th}\) relative to \(^{238}\text{U}\) was observed in three occasions in this thesis. First, bulk regolith samples systematically showed \((^{230}\text{Th} / ^{238}\text{U}) < 1\) in all case studies (Chapters 2, 3 and 4). Second, two out of the three bulk bedrocks analysed displayed depletion in \(^{230}\text{Th}\) relative to \(^{238}\text{U}\) (Chapters 2 and 3). Finally, all quartz separates \((^{230}\text{Th} / ^{238}\text{U})\) activity ratios were lower than unity (Chapters 3 and 4). Preferential mobilization of \(^{230}\text{Th}\) relative to \(^{238}\text{U}\) during weathering was explained by recoil and/or preferential leaching of \(^{230}\text{Th}\) from recoil tracks (Kigoshi, 1971). Note that Th is considered nearly immobile and once dissolved is expected to rapidly re-precipitate (Chabaux et al., 2003). However, Th solubility is enhance by organic ligands in solution; hence, during regolith formation it is possible that organic matter dissolved in soil pore water plays a major role in Th mobilization and translocation from regolith (Bourdon et al., 2003; Chabaux et al., 2003; Cowart and Burnett, 1994; Langmuir and Herman, 1980).

Greater mobility of \(^{238}\text{U}\) relative to \(^{234}\text{U}\) was also observed throughout this thesis. The most remarkable finding was observed in quartz separates of the sandstone weathering profile (Chapter 4). In the bedrock, quartz was in secular equilibrium – i.e. \((^{234}\text{U} / ^{238}\text{U} = 1)\);
during the transition of bedrock into B horizon (i.e. the deepest regolith sample collected) $^{234}$U was preferentially leached relative to $^{238}$U and resulted – as expected – into $(^{234}$U/$^{238}$U) <1. However, throughout the rest of the profile and with decreasing depth the $(^{234}$U/$^{238}$U) increased toward unity, suggesting preferential loss of $^{238}$U relative to $^{234}$U. This was explained using the study by Andersen et al. (2009a). These authors hypothesised a two-step processes occurring during rock leaching. First, during incipient leaching a pool of easily leached U enriched in $^{234}$U relative to $^{238}$U is dissolved. Second, when weathering progresses and this pool is exhausted, $^{238}$U starts being preferentially mobilized relative to $^{234}$U. In the case of quartz separated from the sandstone profile, the first stage corresponds to the transition of bedrock into B horizon and results in decreasing $(^{234}$U/$^{238}$U). The second step reflects preferential loss of $^{238}$U over $^{234}$U with decreasing depth throughout the regolith, resulting in increasing $(^{234}$U/$^{238}$U). In addition, preferential loss of $^{238}$U relative to $^{234}$U was observed in the basaltic weathering profiles (Chapter 2), where sequential extraction and etching of bedrock, saprolite and soil resulted in increasing $(^{234}$U/$^{238}$U).

These findings suggest that isotopic fractionation processes that do not reflect the expected U-series isotope mobility (i.e. $^{234}$U > $^{238}$U > $^{230}$Th) could play a major role in the evolution of U-series isotopic composition during regolith development.

**Implications and future developments**

The findings presented in this thesis should encourage reconsidering the mobility of U-series isotopes in regolith. Interpretation of isotopic composition of weathering profiles could require more awareness of fractionation processes that are currently underrated, such as preferential mobilization of $^{230}$Th relative to $^{238}$U (e.g. Essien, 1990; Romer and Rocholl, 2004; Sheng, 1986; Sheng and Kuroda, 1986a; Shirvington, 1983; Tanaka et al., 2015). Further research is needed to better understand these processes. A possible starting point to better comprehend U-series isotopes mobility during weathering of rock and regolith is the work by Andersen et al. (2009a). They performed an 1100-hour-long leaching experiment on a rock and monitored the $(^{234}$U/$^{238}$U) only of the leaching solution. Future works could analyse $(^{234}$U/$^{238}$U) and $(^{230}$Th/$^{238}$U) in both leaching solution and solid residue. Moreover, similar experiments could be performed on regolith to
investigate differences between U-series isotope mobility occurring during weathering of rock and regolith.

5.4 Concluding remarks

Although regolith production rates inferred using U-series isotopes are commonly estimated on bulk regolith, isolation of bedrock-derived phases offers a solution to simplify this technique. Sequential extraction and mineral separation revealed to be potential tools to achieve this. Isolation of bedrock-derived phases could simplify the model from which regolith production rates are derived by eliminating a preventable assumption; i.e. similar timescale by which nuclides are gained and lost during pedogenesis. The benefit of this methodological improvement could be i) more accurate regolith production rates and ii) improved understanding of U-series isotope fractionation processes at play during regolith formation. On the long-term, this could contribute to our knowledge on weathering rates, landscape evolution and provide information to better comprehend interplays between weathering processes and climate (e.g. Hilley et al., 2010; Raymo and Ruddiman, 1992; West, 2012).
References


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6 Appendix A – Sample preparation

6.1 Sequential extraction

Regolith is composed by several phases, the principal are bedrock-derived, solution-derived and organic matter (see section 1.3). In the first chapter of this thesis, we pointed out how solution-derived secondary phases and organic matter may affect the U-series isotopic composition of soil and saprolite. This reduces the accuracy of modelled regolith production rates. Ideally, solution-derived secondary phases and organic matter can be selectively removed using specific chemical reagents (Tessier et al., 1979). This method is named sequential extraction and was first developed and applied to soil by Tessier et al. (1979). The authors defined a procedure to remove four phases form soil samples.

1. The exchangeable phases. They refer to trance metals adsorbed on regolith grains surface by weak bounds. These fractions are removed varying the ionic composition of the medium (e.g. solution).

2. The acid-soluble phases. They are composed by carbonate minerals, which are known to significantly bound trace elements such as U and Th. These phases are removed by lowering the pH.

3. The reducible phases. They comprise Fe- and Mn- oxides, hydroxides and oxyhydroxides that significantly incorporate large amount of U and Th. These phases are dissolved in solution by reduction reactions.

4. Oxidisable phases. They are mostly represented by organic matter, which can be oxidized and dissolved in solution.

The residue of this procedure incorporates the material that is not removed by the previous steps. Ideally, it contains chiefly primary minerals and resistant secondary phases (e.g. bedrock-derived).

The original procedure, more specifically the chemical reagents and reaction conditions, have been modified by several authors and for different purposes. Focusing on the U-series isotopes, the most important variations were suggested by Schultz et al. (1998), Lee (2009), Suresh et al. (2014) and Martin et al. (2015). Interestingly, Blanco et al. (2004) compared the sequential extraction procedures used by Tessier et al. (1979) and Schultz
et al. (1998) on a soil sample and studied their effect on the U-series isotopes. They found no significant variation in the overall removal of U, while the U distribution among the different phases was different. In this thesis, we adopted the procedure proposed by Lee (2009), which is directly based on the protocol by Schultz et al. (1998) and is showed in Table 6.1.

Table 6.1 Procedure for sequential extraction. All reagent volumes are intended for 1 g of sample

<table>
<thead>
<tr>
<th>Phase aimed at</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Exchangeable</td>
<td>8 mL of 1 M Mg(NO$_3$)$_2$. Agitate at room temperature for 50 min.</td>
</tr>
<tr>
<td>2) Acid-soluble</td>
<td>16 mL of 1 M NaOAc at pH 5 (adjusted with AcOH). Agitated at room temperature for 5 hr.</td>
</tr>
<tr>
<td>3) Reducible</td>
<td>20 mL 0.04 M NH$_2$OH·HCl/AcOH (pH 2). At 96 °C for 5 hr and agitated occasionally.</td>
</tr>
<tr>
<td>4) Oxidisable</td>
<td>- 3 mL of 0.02 M HNO$_3$ + 5 mL 30% H$_2$O$_2$ at pH 2 (adjusted with HNO$_3$), at 85 °C for 2 hr and occasionally agitated.</td>
</tr>
<tr>
<td></td>
<td>- 3 mL 30% H$_2$O$_2$, pH 2 (adjusted with HNO$_3$), at 85 °C for 3 hr and occasionally agitated.</td>
</tr>
<tr>
<td></td>
<td>- 5 mL of 3.2 M NH$_4$OAc in 20% HNO$_3$, diluted up to 20 mL with H$_2$O, agitated at room temperature for 30 min.</td>
</tr>
</tbody>
</table>

The five steps were carried out in PFA centrifuge tubes. At the end of each step, the reagent was removed after centrifugation, using a Pasteur pipette. The sample was rinsed with 14 ml of deionized water twice, and the solution was removed after centrifugation using a Pasteur pipette.

### 6.2 Acid dissolution

In order to analyse U-series isotopic composition and elements concentrations (with the exception of Si), rock and regolith samples were dissolved by standard acid dissolution methods – all reagent are Suprapur® grade. In Chapters 2 and 3, perchloric acid (HClO$_4$) was employed with the aim of minimizing the formation of insoluble fluorides, which
may prevent total dissolution of trace elements including U and Th during HF digestion of geological samples; in this cases, recommendations by Yokoyama et al. (1999) were followed. In Chapter 4, 69% HNO₃ was used instead of HClO₄ for safety reasons. In this thesis, dissolution was performed on ~100 mg of sample (pre-weighted). A known mass of tracer containing 1.04 ppb of ²²⁹Th and 0.429 ppb of ²³⁶U was used for the concentration analyses of U and Th on the MC-ICP-MS. The sample was dissolved using a solution of 2.5 ml 32% HF and 0.5 ml 70% HClO₄ (Chapters 2 and 3) or a solution of 2.5 ml 32% HF and 0.5 ml 69% HNO₃ (Chapter 4), at 100 ºC overnight and then dried. The sample was re-dissolved in 3 ml 32% HCl – if necessary, H₃BO₃ was added in order to dissolve possible fluorides – and heated at 80 ºC overnight and finally dried. The latter step was repeated once. Following this, the sample was dissolved in 0.5 ml 69% HNO₃ and dried; this step was repeated twice. The residue was dissolved in 1.5 M HNO₃; an aliquot was used for chromatography and U-series isotopic analyses, while a second aliquot was dried down, dissolved in 2% HNO₃ and used for possible elemental analyses. All reagents were Suprapur grade (Merck) and dilutions were made using deionized water. Overall, the author has found the HF-HClO₄ dissolution recommended by Yokoyama et al. (1999) effective as no insoluble fluorides were observed.

6.3 Chromatography

For the determination of U and Th concentrations, and U-series isotopes activity ratios we used a Multi-Collector ICP-MS. This instrument suffers of instrumental mass fractionation (i.e. mass bias) and may be subject of isobaric interferences caused by the presence of other isotopes in the matrix (this topic is described in details later in the text). These issues are minimized by isolating U on the one hand and Th on the other hand, via ion exchange chromatography.

Ion exchange chromatography is a technique in which a mobile phase (i.e. digested sample) flows inside a column filled with a solid phase, namely an ion-exchange resin. When the mobile and solid phases are in contact they exchange ions; an ion-exchange resin is chosen because it strongly binds one or more elements, while all the others are easily eluted (washed out). We selected an ion-exchange resin that strongly binds U and Th. Once U and Th are isolated in the resin, they are separately eluted and collected using
specific solvents. The results are two solutions, one containing ideally only U and the other Th.

In this thesis, the ion exchange resin used is *Eichrom TRU resin*, in which the extractant system (columns) is octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide dissolved in tri-n-butyl phosphate (Horwitz et al., 1993). In addition, *Eichrom pre-filter resin* was employed (Part Number PF-C50-A). The columns used for chromatography are polypropylene spin columns with 1.2 ml bed-volume (Bio-Spin® #7326025). First, columns were rinsed with ethanol and deionized water before 0.1 ml of pre-filter resin and 0.5 ml of TRU resin were added. The chromatography procedure is described in Table 6.2 – note that the introduced sample is dissolved in 1.5 M HNO₃. At the end of chromatography, U and Th were eluted into 0.5 M HCl and 0.1M HCl - 0.3M HF respectively. Samples were dried, then 0.5 ml 31% H₂O₂ (Suprapur, Merck) were added and they were dried again; this was done to remove any organic material (e.g. derived from the resin). Following this, the sample was dissolved in 4 ml 2% v/v HNO₃.
Table 6.2. Procedure for ion exchange chromatography. Note that each reagent addition to columns cannot exceed 2 ml (column capacity). All reagents are Suprapur grade (Merck) and diluted with deionized water.

<table>
<thead>
<tr>
<th>Cleaning</th>
<th>2+2+2 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M HCl</td>
<td></td>
</tr>
<tr>
<td>0.5M HCl</td>
<td></td>
</tr>
<tr>
<td>0.1M HCl - 0.3M HF</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Preconditioning</th>
<th>2+2+2+2+1 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5M HNO₃</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Load sample</th>
<th>2 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5M HNO₃</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wash</th>
<th>2+2+0.5 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5M HNO₃</td>
<td></td>
</tr>
<tr>
<td>3M HCl</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collect Th in clean vial</th>
<th>2+2+0.5 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M HCl</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collect U in clean vial</th>
<th>2+2+2+2 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M HCl - 0.3M HF</td>
<td></td>
</tr>
</tbody>
</table>
7 Appendix B – Sample analyses

7.1 MC-ICP-MS

Recent development of multi-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS) techniques made possible the precise measurement of isotopic ratios of U-series isotopic ratios. In the course of this thesis, we analysed the U-series isotopic composition using a Thermo Fisher Scientific Neptune Plus™ MC-ICP-MS. This instrument is composed by five major parts: i) sample inlet system; ii) inductively-coupled-plasma (ICP); iii) mass spectrometer interface; iv) mass analyser; and v) multi-collector.

In the sample inlet system, a liquid (or gas) sample is constantly introduced in a nebulizer where it mixes with Ar gas and forms an Ar-sample aerosol. The sizes of the aerosol particles need to be controlled in order to maximize the ionization efficiency of the plasma; this is done by passing the aerosol through a spray chamber. Alternatively, inlet systems equipped with heated cyclonic spray chamber can be used (e.g. High Sensitivity Sample Introduction System Apex Q). In this thesis an Elemental Scientific Apex Q has been employed. The aerosol is then transferred to the plasma.

The inductively-coupled plasma is formed and retained in a torch constituted by a load coil. The load coil is made of three turns of copper tubing on which a radio frequency (RF) power is applied. This produces an electromagnetic field around the torch in which electrons are seeded and accelerated. When Ar gas is introduced in the torch, its atoms collide with the electrons and ionize. Argon ionization results in the release of additional electrons, which in turn ionize more Ar atoms and produce self-sustained plasma. Electrons, neutral Ar and Ar+ ions form the plasma, which riches temperature of about 8000 °C. The aerosol particles containing the sample are introduced in the plasma; they dehydrate, vaporize and are atomized. Once the sample atoms are formed, they collide with the electrons in the plasma and finally ionize. At this stage, the sample is ionized at high temperature and atmospheric pressure.

The mass spectrometer interface is mainly made of two metal discs with a small hole in the centre (~ 1 mm) – called sampler cone and skimmer cone. Their main purpose is to i)
sample the central part of the ion beam generated in the torch, and ii) drop the pressure from atmospheric, in the plasma, to near-vacuum, in the analyser. Following the spectrometer interface, in the transfer lens system the pressure is pumped down to $<10^{-7}$ mbar and the ion beam is focused and accelerated toward the mass analyser.

The mass analyser has the purpose of shaping, focusing and controlling the kinetic energy of the ion beam coming from the mass spectrometer interface. The ions coming from the skimmer cone are first extracted by a system of lenses, which shape and direct the ion beam toward the mass analyser. The mass analyser is composed by two main parts which use an electrostatic and a magnetic field respectively to focus the ion beam on the multi-collectors.

The multi-collector is composed by eight detectors – on which Faraday cups and/or ion counting detectors can be installed – and one fixed central Faraday cup. In total, a multi-collector can be equipped with nine Faraday cups and eight ion counting detectors. Each collector is mechanically moved in order to be positioned on the trajectory of a selected ion beam. During our measurements, the fixed central cup was equipped with a Retarding Potential Quadrupole Lens (RPQ) and a Secondary Electron Multiplier (SEM). This setting removes ions that have been affected by energy loss due to scattering occurred during their transfer through the mass spectrometer. The adoption of an RPQ and SEM results in lower background signal and increased abundance sensitivity of the instrument. In turn, this produces better defined intensity peaks (i.e. smaller tails).

### 7.1.1 Instrument setup

For U-series analyses we used a Thermo Fisher Neptune plus MC-ICP-MS at The Australian National University, Canberra. The instrument was equipped with:

- Jet-cone mounted at the MS interface for increased sensitivity
- Standard skimmer cone
- RPQ-SEM
- ESI Apex-Q inlet system

The plasma was turned on and allowed to stabilize before the instrument was tuned. We used a tuning solution containing U and/or Th at concentration of 2-20 ppb to optimize
ion beam intensity and peak shape. The optimization was achieved primarily adjusting the ICP torch position, sample gas flow rates, and transfer lenses. Typical sample gas flow was ~1 L/min.

Once the ion beam intensity and peak shape were optimized, the collector position was set. We used two different collector position settings, one for U and another for Th:

- For U, mass 238 and 235 were analysed in the Faraday cups, while masses 234, 236, 236.5 and 235.5 were analysed in ion counting detectors (for more detail see tail correction section reported below).
- For Th, mass 232 was analysed in the Faraday cup, while masses 230, 229, 231.5, 230.5, 229.5 and 228.5 were analysed in ion counting detectors (for more detail see tail correction section reported below).

### 7.1.2 Mass bias correction

Mass bias, also referred to as instrumental mass fractionation, is a major issue of analyses performed on MC-ICP-MS. To comprehend the concept of mass bias we first need to understand the notion of isotope transmission through an ICP-MS. The transmission, T, for a certain isotope, $M_i$, is the ratio between the number of ions of $M_i$ detected by the instrument ($I_{M_i,detected}$) and the number of atoms of $M_i$ introduced in the instrument ($A_{M_i,introduced}$):

$$T_{M_i} = \frac{I_{M_i,detected}}{A_{M_i,introduced}}$$

The transmission through a MC-ICP-MS varies between isotopes of the same element and creates uncertainties in the measurement of an isotopic ratio. Two major factors cause instrumental mass fractionation: sample ionization in the plasma, and transfer of the ion beam from the plasma to the mass analyser (Albarède and Beard, 2004). In general, the most remarkable cause is the mass fractionation that occurs in the plasma. In this thesis, mass bias was corrected using standard bracketing.

Standard bracketing is a mathematical method to infer mass bias on a certain isotopic ratio of an unknown sample, produced during MC-ICP-MS analyses. This is done by
analysing the isotopic composition of a standard before and after the unknown sample. When the isotopic ratio (e.g. $^{234}\text{U}/^{238}\text{U}$) of a standard solution is known, the mass bias produced during the analysis can be assessed by analysing the standard solution and comparing the true and the measured isotopic ratios. If the mass bias varies smoothly during an analytical session, the bias of an unknown sample can be interpolated between the biases assessed for two standards, one run before and one after the sample:

$$R_{x,\text{Sample}} = \frac{R_{x,\text{std}} \times r_{x,\text{Sample}}}{\sqrt{r_{x,\text{std1}} - r_{x,\text{std2}}}}$$

where $R_{x,\text{Sample}}$ is the mass-bias corrected value for the isotopic ratio $x$; $R_{x,\text{std}}$ is the true isotopic composition of the standard; $r_{x,\text{Sample}}$ is the measured isotopic ratio of the sample and $r_{x,\text{std1}}$, $r_{x,\text{std2}}$ are the measured isotopic ratios of the standards analysed before and after the sample. The standard solutions used for the analyses carried in this thesis were synthetic standard CRM U010 for U and OU Th”U” for Th. As mentioned above, to use standard bracketing it is necessary that mass bias varies smoothly between standards and samples. This type of variation is characteristic of MC-ICP-MS, on the condition that the sample is purified and its matrix minimized. This is one of the reasons why ionic exchange chromatography was employed.

### 7.1.3 Memory effect minimization

Memory effect is produced during an analytical session when analyte elements from precious samples are accumulated in the instrument and contribute to the signal measured on following samples. This can be the result of uptake of sample on different parts of the ICP-MS, such as uptake tubing, nebulizer and spray chamber. Memory effect is minimized by flushing the system thoroughly with a solution of 0.1% v/v Triton™ X-100 in 2% HNO$_3$ for U analyses, and 0.1% v/v Triton™ X-100 + 0.05% v/v HF in 2% HNO$_3$ for Th.

### 7.1.4 Tail correction

Tail effect is the contribution to the signal measured for a mass of interest generated from a different mass. For instance, because the concentration of $^{238}\text{U}$ in natural samples is several orders of magnitude higher than $^{236}\text{U}$, $^{238}\text{U}$ produces a tail that contributes to the
signal detected for $^{236}\text{U}$. Similarly, $^{232}\text{Th}$ produces a tail that affects the signal of $^{229}\text{Th}$ and $^{230}\text{Th}$. To obtain accurate measurement of $^{236}\text{U}$, $^{229}\text{Th}$ and $^{230}\text{Th}$, the tail must be corrected.

In this thesis, the tail of $^{238}\text{U}$ (238 atomic mass unit; i.e. $am\mu$ throughout this text) on $^{236}\text{U}$ (236 amu) is estimated interpolating the intensities measured at 235.5 and 236.5 amu; the value is subsequently subtracted from the intensity measured for $^{236}\text{U}$. This implies that $^{236}\text{U}$ generates negligible tail at 235.5 and 236.5 amu. Similarly, the tail of $^{232}\text{Th}$ on $^{229}\text{Th}$ (229 amu) and on $^{230}\text{Th}$ (230 amu) are estimated by interpolating the intensities measured at 231.5, 230.5, 229.5 and 228.5 amu, and subtracted to the measured $^{229}\text{Th}$ and $^{230}\text{Th}$ intensities, respectively.

7.1.5 Isotopic dilution to calculate U and Th concentrations

The concentration of U and Th – intended as concentrations of $^{238}\text{U}$ and $^{232}\text{Th}$ – were assessed by isotopic dilution. A known mass of a spike containing $^{236}\text{U}$ and $^{229}\text{Th}$ and of known isotopic composition was added to each sample. The concentration of $^{238}\text{U}$ and $^{232}\text{Th}$ were calculated using measured $^{236}\text{U}/^{238}\text{U}$ and $^{229}\text{Th}/^{232}\text{Th}$ ratios.

7.1.6 Accuracy and precision

Sample preparation procedures, such as acid dissolution and chromatography, may produce isotopic fractionation and thus affect data accuracy. Accuracy was assessed by processing (dissolution, chromatography etc.) and analysing one rock standard QLO-1 (U.S. Geological Survey) – which is known to be in secular equilibrium – every ten samples. Table 7.1 shows that measured U and Th concentrations are within error of recommended values (Abbey and Canada, 1983; Flanagan and Flanagan, 1976; Govindaraju, 1994). The average ($^{234}\text{U}/^{238}\text{U}$) activity ratio is within error of secular equilibrium, while considering the error, the average ($^{230}\text{Th}/^{238}\text{U}$) is slightly lower than the expected value (0.998).

Precision was assessed for each analysis session by measuring synthetic standard CRM U005-A for U and UCSC ThA for Th; reference values are reported in Table 7.2.

Table 7.1. Thorium and uranium concentrations, ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios for the analysed rock standard USGS QLO-1. Errors reported for average values are propagated 2 Standard errors.
<table>
<thead>
<tr>
<th>Date of preparation</th>
<th>Th (ppm)</th>
<th>2SE</th>
<th>U (ppm)</th>
<th>2SE</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>2SE</th>
<th>$^{230}\text{Th}/^{238}\text{U}$</th>
<th>2SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>14-Dec-13</td>
<td>4.67</td>
<td>0.01</td>
<td>1.80</td>
<td>0.01</td>
<td>1.004</td>
<td>0.002</td>
<td>1.008</td>
<td>0.007</td>
</tr>
<tr>
<td>23-Jan-14</td>
<td>4.63</td>
<td>0.00</td>
<td>1.80</td>
<td>0.01</td>
<td>0.998</td>
<td>0.009</td>
<td>0.952</td>
<td>0.011</td>
</tr>
<tr>
<td>07-Feb-14</td>
<td>4.90</td>
<td>0.01</td>
<td>1.88</td>
<td>0.02</td>
<td>1.001</td>
<td>0.008</td>
<td>0.900</td>
<td>0.013</td>
</tr>
<tr>
<td>14-Mar-14</td>
<td>4.87</td>
<td>0.00</td>
<td>1.92</td>
<td>0.00</td>
<td>1.001</td>
<td>0.002</td>
<td>0.974</td>
<td>0.006</td>
</tr>
<tr>
<td>01-Apr-14</td>
<td>4.69</td>
<td>0.01</td>
<td>1.84</td>
<td>0.00</td>
<td>1.003</td>
<td>0.002</td>
<td>0.978</td>
<td>0.007</td>
</tr>
<tr>
<td>07-May-14</td>
<td>4.74</td>
<td>0.01</td>
<td>1.87</td>
<td>0.01</td>
<td>1.003</td>
<td>0.002</td>
<td>0.983</td>
<td>0.007</td>
</tr>
<tr>
<td>20-May-14</td>
<td>4.71</td>
<td>0.01</td>
<td>1.84</td>
<td>0.00</td>
<td>1.004</td>
<td>0.003</td>
<td>0.983</td>
<td>0.006</td>
</tr>
<tr>
<td>20-May-14</td>
<td>4.80</td>
<td>0.01</td>
<td>1.88</td>
<td>0.00</td>
<td>1.002</td>
<td>0.002</td>
<td>0.970</td>
<td>0.007</td>
</tr>
<tr>
<td>23-Jul-14</td>
<td>4.34</td>
<td>0.01</td>
<td>1.87</td>
<td>0.00</td>
<td>1.003</td>
<td>0.001</td>
<td>0.917</td>
<td>0.007</td>
</tr>
<tr>
<td>04-Dec-14</td>
<td>5.00</td>
<td>0.01</td>
<td>1.93</td>
<td>0.01</td>
<td>1.003</td>
<td>0.002</td>
<td>1.042</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Average 4.73 0.02 1.86 0.03 1.002 0.014 0.971 0.027

Table 7.2. Synthetic standard values and respective standard deviations (2 SD).

<table>
<thead>
<tr>
<th>U005A</th>
<th>ThA</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}\text{U}/^{238}\text{U}$</td>
<td>3.419E-05</td>
<td>-</td>
</tr>
</tbody>
</table>
Blank controls are taken to assess possible contamination during sample preparation and analysis. Total procedure blanks were carried out for each sample batch and approximately every ten samples. Table 7.3 reports the masses of U and Th yielded for each blank. The values are relatively low, except for the batches prepared on February and March 2014, when both U and Th yields were significantly high due to laboratory contamination issues. If the two batches processed in February and March 2014 are excluded, the maximum blank contribution to the mass of U in samples is 0.2%. The batch processed in February shows blank contributions comprised between 0.1 and 0.6% (average 0.2%, n=10) with only two samples exceeding 0.3%. The batch prepared on March 2014 shows blank contributions between 0.3 and 3.5% (average 0.8%, n=9), with only one sample exceeding 0.1%.

Similarly, excluding the batch processed in February 2014, the maximum percentage of blank contribution to the mass of Th contained in samples is 0.1%. The batch prepared in February 2014 shows blank contributions between 0.3 and 3.5% (average 0.8%, n=10), with only three samples exceeding 1.5%. The high blank contribution is due to the combination of great Th concentrations in the blank and low in samples (quartz separates).

<table>
<thead>
<tr>
<th></th>
<th>2SD</th>
<th>235U/238U</th>
<th>2SD</th>
<th>236U/238U</th>
<th>2SD</th>
<th>230Th/232Th</th>
<th>2SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2SD</td>
<td>4.6E-08</td>
<td>-</td>
<td>5.09E-03</td>
<td>-</td>
<td>5.1E-06</td>
<td>5.855E-06</td>
<td>-</td>
</tr>
<tr>
<td>235U/238U</td>
<td>1.98E-05</td>
<td>-</td>
<td>1.00E-08</td>
<td>-</td>
<td>1.00E-08</td>
<td>8.2E-08</td>
<td>(Rubin, 2001)</td>
</tr>
</tbody>
</table>

7.1.7 Blank controls taken to assess possible contamination during sample preparation and analysis. Total procedure blanks were carried out for each sample batch and approximately every ten samples. Table 7.3 reports the masses of U and Th yielded for each blank. The values are relatively low, except for the batches prepared on February and March 2014, when both U and Th yields were significantly high due to laboratory contamination issues. If the two batches processed in February and March 2014 are excluded, the maximum blank contribution to the mass of U in samples is 0.2%. The batch processed in February shows blank contributions comprised between 0.1 and 0.6% (average 0.2%, n=10) with only two samples exceeding 0.3%. The batch prepared on March 2014 shows blank contributions comprised between 0.3 and 3.5% (average 0.8%, n=9), with only one sample exceeding 0.1%.

Similarly, excluding the batch processed in February 2014, the maximum percentage of blank contribution to the mass of Th contained in samples is 0.1%. The batch prepared in February 2014 shows blank contributions between 0.3 and 3.5% (average 0.8%, n=10), with only three samples exceeding 1.5%. The high blank contribution is due to the combination of great Th concentrations in the blank and low in samples (quartz separates).

Table 7.3 Masses of U and Th analysed in total procedure blanks. BID referrers to below instrument detection.
<table>
<thead>
<tr>
<th>Date of preparation</th>
<th>Th (pg)</th>
<th>U (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>03-Oct-13</td>
<td>185</td>
<td>43</td>
</tr>
<tr>
<td>17-Oct-13</td>
<td>239</td>
<td>16</td>
</tr>
<tr>
<td>17-Oct-13</td>
<td>161</td>
<td>23</td>
</tr>
<tr>
<td>14-Dec-13</td>
<td>214</td>
<td>37</td>
</tr>
<tr>
<td>07-Jan-14</td>
<td>105</td>
<td>53</td>
</tr>
<tr>
<td>23-Jan-14</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>07-Feb-14</td>
<td>1396</td>
<td>39</td>
</tr>
<tr>
<td>14-Mar-14</td>
<td>75</td>
<td>297</td>
</tr>
<tr>
<td>01-Apr-14</td>
<td>907</td>
<td>124</td>
</tr>
<tr>
<td>07-May-14</td>
<td>140</td>
<td>84</td>
</tr>
<tr>
<td>20-May-14</td>
<td>91</td>
<td>87</td>
</tr>
<tr>
<td>14-Jul-14</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>04-Dec-14</td>
<td>Bid</td>
<td>Bid</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>294</strong></td>
<td><strong>68</strong></td>
</tr>
</tbody>
</table>

### 7.2 ICP-MS

In this thesis, we used an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) for elemental concentration analyses. This instrument can measure the concentration of most of the elements contained in the periodic table with detection limits at or below the part per billion (ppb) and handles virtually any type of matrix.

The sample introduction system, ICP torch and interface systems (sampler and skimmer cones) of an ICP-MS are very similar to the ones previously described for a MC-ICP-MS. A liquid sample is nebulized, mixed with Ar gas and injected into the plasma, where it
ionizes at high temperature and atmospheric pressure. The interface system (sampler and skimmer cones) focuses the ions into a beam and drops the pressure to near-vacuum. A lens system focuses and shapes the ion beam into the mass spectrometer. The mass spectrometer is the component of the ICP-MS that separates the ions from each other on the basis of their mass/charge ratio. Three types of mass spectrometers are commonly used in laboratories: quadrupole, time-of-flight and magnetic sector. We used an ICP-MS equipped with a quadrupole system.

A quadrupole, also referred to as a mass analyser, consists of four rods approximately 20 cm long and 1 cm in diameter, set parallel to each other. When an ion beam exits the ion lens system, it enters the quadrupole and only ions with a specific mass/charge (m/z) ratio are allowed to pass through. The m/z ratio is set by selecting the right voltage and radio-frequencies of the quadrupole. All the ions that do not have the selected m/z ratio pass in between the quadrupole rods and are not collected by the ICP-MS. An important characteristic of the ICP-MS is that the voltage and radio frequency of the quadrupole can be quickly changed and set to select any m/z ratio. This enables, for each sample introduced in the instrument, to scan and analyse virtually every isotope in a very short time (minutes). The ions exiting the quadrupole are then directed toward the detector.

The detector is a system that converts the signal produced by an ion striking its surface into an electric signal. The signal is amplified until a measurable pulse is created. Pulses are counted and the instrument returns the number of ions that have stricken the detector, commonly measured in counts-per-seconds (cps). Therefore, for a sample introduced in the instrument, the cps of most of the isotope of the periodic table can be determined in few minutes.

Our analyses were performed using an Agilent 7500 ICP-MS at University of Wollongong, Australia. The analyses were carried out on an aliquot of dissolved sample prior to ion exchange chromatography. Samples were diluted in 2% v/v HNO₃ in order to achieve a concentration of the elements of interest in the range of the calibration standards (between 0.005 and 500 ppb). The concentrations were determined using 8-12 standards, with concentrations ranging between 0.005 and 500 ppb, and constructing a calibration curve.
7.2.1 Internal standardization

Internal standardization is used to correct for signal drift and matrix effect (i.e. non-spectral interferences), and results in improved analytical accuracy and precision. Signal drift is defined as gradual decrease of an analyte signal in time during an analysis session and is believed to occur due to deposition of sample-matrix components on the orifices of sampling and skimmer cones (Takahashi, 2014). Sample matrix can produce signal suppression or enhancement depending on the element analysed. These issues are commonly corrected using an internal standard which contain element(s) that i) are not expected in the sample and ii) with atomic number similar to the element(s) of interest (Vanhaecke et al., 1992). In the case of our analyses, an identical amount of an internal standard containing scandium (Sc), indium (In), bismuth (Bi) and Yttrium (Y) was added to all samples, blanks and calibration standards. The signal of each element of interest is normalised to the signal of the element in the internal standard with the closest mass to the element of interest; for instance, K, Ca and Ti were normalized to Sc.

7.2.2 Spike recovery

Spike recovery is commonly used to assess whether the detection of analyte elements is affected by the difference between the matrix of samples and of the calibration standards. Every ten samples, a known mass of spike containing the elements of interest is added to a known mass of a randomly duplicated sample. Spike addition is done in order to significantly increase the analyte element concentration in the sample, by 50-100%, albeit remaining within the calibration curve range. To calculate spike recovery, first, the expected concentration of the spiked sample is calculated using the measured concentrations of the original sample and of the spike. Second, spike recovery is calculated as the ratio of the measured to the expected concentrations of the spiked sample in percent. A recovery comprised between 90 and 110% is usually considered appropriate. The range of spike recoveries for the analysed elements is comprised between 96 and 111%. Therefore, the matrix effect is regarded to have not significant effect on samples.

7.2.3 Standard quality control

Quality control standard checks are run once every circa ten samples to assess memory effect. This effect was minimized by flushing the system with solutions of 0.1% v/v
Triton™ X-100 dissolved in 2% v/v HNO₃ between sample analyses. Because of the effective flushing procedure and relatively short analysis session (normally comprising <40 samples), the memory effect was negligible in our analyses.

### 7.2.4 Blanks

One total procedure blank was processed and analysed for every batch of ten samples. For Na, Mg and K, most of the blank concentrations were within instrument background noise. Because sample concentrations were several orders of magnitude greater than that, contamination was assumed negligible. However, two batches show blanks with high Na content and one batch with high K. The blank contribution to the mass of Na in samples is between 0.02 and 3.4% (average 1.6%, n= 13), while for K it is between 0.1 and 2.4% (average 1.8, n=8). The data contained in the batch showing these blanks are accepted because major element concentrations are used for semi-quantitative comparison among samples. For the other elements, the maximum blank contribution to the mass of Mg, Al, Ti, Mn, Fe and Zr of samples is 0.4, 0.02, 0.002, 0.001, 0.002 and 0.01%, respectively.

### 7.2.5 Analytical uncertainty

Rock standards USGS QLO-1 were processed and analysed every approximately ten samples to assess analytical uncertainty. For Na, Mg, Al and Ti the uncertainty was better than 8, 6, 11 and 9%, respectively. For Fe, analytical uncertainty is better than 6% except for a standard that shows 13%. Similarly, K displays uncertainties better than 8%, except for a batch that displays 30%. Zirconium shows values <7%, except for two standards that show 11 and 14%. Some of these values are high; this may produce semi-quantitative data. Because in this thesis element concentrations are used to assess variations among samples, semi-quantitative data are acceptable.

### 7.3 X-ray Fluorescence

X-ray fluorescence (XRF) spectrometry is a rapid and common analytical technique used to analyse major and trace element concentrations on relatively large amount of samples (i.e. ~10 g). In this thesis, XRF were used to analyse bulk and leached rock and regolith. In contrast, for mineral separates (i.e. quartz and biotite) only few hundreds of grams were available and ICP-MS analyses were preferred.
In an XRF instrument, X-rays are produced and directed onto a sample. The X-rays excite sample elements by ejecting one or more electrons from their low-energy inner orbitals (i.e. ionization). The atom electrons are then rearranged and an electron located in a highly energetic outer orbital replaces the one lost. Because the energy difference between the inner and outer orbitals, this process releases energy into the form of electromagnetic radiation. The radiation wavelengths are characteristic for each atom and can be used to identify elements. The XRF analysis of a geologic sample implies the production of a complex radiation spectrum due to the presence of several elements. The instrument divides the spectrum in wavelengths that are characteristic for each element. The intensity of each wavelength is proportional to the concentration of the element; hence the XRF returns a quantitative elemental analysis of a sample.

In this thesis, major element compositions of bulk and leached samples were determined using fused discs on a Tracor Northern energy dispersive X-ray fluorescence (XRF) analyser with automated, computer-driven data collection and processing, at University of Wollongong. The analytical uncertainty of XRF analyses was estimated using internal standards and was ±4% for Na₂O, ±20% for SO₃ and < ± 1% for the other oxides.

7.4 X-ray Diffraction

X-ray diffraction (XRD) is an analytical method used to identify crystalline solids and can also provide semi-quantitative mineralogical analyses. In this thesis, it was used to estimate regolith and bedrock mineralogy.

In an XRD instrument, monochromatic X-rays interact with a powdered sample and are scattered in different directions, producing destructive and constructive interferences. The intensity of the rays scattered at different angles are measured and recorded into a diffractogram. The powder of a crystalline material has a characteristic X-ray diffraction pattern which is used to identify it. Moreover, using specific softwares (e.g. siroquant) it is possible to estimate the mineral concentration of a sample.

The XRD measurements were made on samples crushed to particles <10 μm using a Tollmill crusher (TEMA). The powdered samples were mounted on holders and analysed with a Phillips 1130/90 diffractometer set to 35 kV and 28.8 mA. A Spellman DF3
generator was set to 1 kW and samples were analysed using an automatic sample holder. The analyses were performed with 2-theta values between 4 and 70° at 2° per minute and a step size of 0.02. The data were then processed through GBC 122 control system, and Traces and SIROQUANT softwares. The accuracy obtained by XRD routine analysis is normally about ± 3% at the 95% confidence level (Hillier, 2000).
8 Appendix C – Weathering profiles photographs

8.1 Basaltic weathering profile – Chapter 2

Figure 8.1 Core showing the top meter of the basaltic weathering profile collected at in Exeter, New South Wales, Australia (34°37'15.05" S 150° 19'08.30" E). Samples SUP and SLOW have been extracted from this core.

Figure 8.2 Second core extracted from the basaltic weathering profile, between 1 m and 1.85 m of depth (the upper 15 cm of the core contain debris falled during drilling operations, which have been removed).
8.2  Granitic weathering profile – Chapter 3

Figure 8.4 Granitic weathering profile sampled for the second study (Chapter 3). This profile is located in Crookwell, NSW Australia (34°26′42.67″S 149°12′1.28″E; 734 AMSL). In this study, two soils were collected at
0.3 and 0.9 m of vertical depth (darker area) and three saprolites were collected at 2, 2.2 and 2.5 m of depth (lighter area).

Figure 8.5 Boulders from which the bedrock sample in Chapter 3 was collected. These rocks had been extracted during roadworks occurred few months before the fieldwork.

Sandstone weathering profile – Chapter 4

Figure 8.6 Core showing the top meter of the sandstone weathering profile collected at in Tolwong in the Southern Highlands, New South Wales, Australia (34°51'37.80"S, 150° 7'40.35"E). The two samples of the E horizon have been extracted from this core at 20 and 40 cm.
Figure 8.7 Second core extracted from the sandstone weathering profile, between 1 and 1.8 m of depth. The two B horizon samples have been collected from this core. Note that the upper 15 cm of the core (in the picture the left side) contain soil that has fallen into the borehole during drilling operation; they have not been accounted.
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