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Evaluating the removal of non-detrital matter from soils and sediment using uranium isotopes

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Abstract

The time elapsed since detrital minerals were reduced to $< 63 \mu\text{m}$ by weathering can be constrained by applying the comminution dating method, which is based on the $(^{234}\text{U}/^{238}\text{U})$ activity ratio and surface area properties of the detrital minerals. In order to constrain an accurate age, the detrital minerals should be isolated and non-detrital matter present must be completely removed. Here we evaluate current sample pre-treatment procedures for removing non-detrital matter using uranium isotopes. The $(^{234}\text{U}/^{238}\text{U})$ activity ratio of the solid residue decreased stepwise throughout sequential extraction procedures, which is attributed to the removal of non-detrital matter. Despite the heterogeneity observed in the untreated samples, the final $(^{234}\text{U}/^{238}\text{U})$ activity ratio of solid residues from replicate experiments were within analytical error. This shows that the $(^{234}\text{U}/^{238}\text{U})$ activity ratio of the detrital minerals is consistent following removal of non-detrital matter. The addition of a complexing agent (sodium citrate) to extraction reagents decreased the readsorption of uranium, but did not affect the final $(^{234}\text{U}/^{238}\text{U})$ activity ratio. Mild HF/HCl etching experiments showed that the $(^{234}\text{U}/^{238}\text{U})$ activity ratio can be further decreased following sequential extraction. Particle-size distribution measurements revealed that the decrease in the $(^{234}\text{U}/^{238}\text{U})$ activity ratio is likely due to the dissolution of clay minerals. Mild HF/HCl etching of a rock standard also revealed a small amount of preferential leaching of ^{234}U ($< 1\%$). The inferred comminution ages are generally beyond the limit of the technique (1000 ka). By assuming an initial activity ratio of 0.95 to account for preferential leaching effects, the ages of samples following sequential extraction were within analytical error. Mild HF/HCl etching following sequential extraction results in older ages, which is attributed to the further removal of clay minerals. We recommend sequential extraction followed by mild HF/HCl etching as sample pre-treatment for comminution dating studies.

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Medicine and Health Sciences | Social and Behavioral Sciences

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**Evaluating the removal of non-detrital matter from soils and sediment
using uranium isotopes**

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Abstract

The time elapsed since detrital minerals were reduced to $<63\ \mu\text{m}$ by weathering can be constrained by applying the comminution dating method, which is based on the $(^{234}\text{U}/^{238}\text{U})$ activity ratio and surface area properties of the detrital minerals. In order to constrain an accurate age, the detrital minerals should be isolated and non-detrital matter present must be completely removed. Here we evaluate current sample pre-treatment procedures for removing non-detrital matter using uranium isotopes. The $(^{234}\text{U}/^{238}\text{U})$ activity ratio of the solid residue decreased stepwise throughout sequential extraction procedures, which is attributed to the removal of non-detrital matter. Despite heterogeneity observed in the untreated samples, the final $(^{234}\text{U}/^{238}\text{U})$ activity ratio of solid residues from replicate experiments were within analytical error. This shows that the $(^{234}\text{U}/^{238}\text{U})$ activity ratio of the detrital minerals is consistent following removal of non-detrital matter. The addition of a complexing agent (sodium citrate) to extraction reagents decreased the readsorption of uranium, but did not affect the final $(^{234}\text{U}/^{238}\text{U})$ activity ratio. Mild HF/ HCl etching experiments showed that the $(^{234}\text{U}/^{238}\text{U})$ activity ratio can be further decreased following sequential extraction. Particle-size distribution measurements revealed that the decrease in the $(^{234}\text{U}/^{238}\text{U})$ activity ratio is likely due to the dissolution of clay minerals. Mild HF/ HCl etching of a rock standard also revealed a small amount of preferential leaching of ^{234}U ($<1\%$). The inferred comminution ages are generally beyond the limit of the technique (1000 ka). By assuming an initial activity ratio of 0.95 to account for preferential leaching effects, the ages of samples following sequential extraction were within analytical error. Mild HF/ HCl etching following sequential extraction results in older ages, which is attributed to the further removal of clay minerals. We recommend sequential extraction followed by mild HF/ HCl etching as sample pre-treatment for comminution dating studies.

Keywords: uranium; uranium-series isotopes; comminution age; sequential extraction.

1. Introduction

The uranium-series (U-series) isotopes are fractionated by chemical and physical weathering, and undergo radioactive decay on timescales relevant to Earth-surface processes (10^3 – 10^6 a). The *comminution dating* technique is a developing application of the U isotopes, which calculates the time elapsed since fine-grained, detrital minerals were reduced to $<63\ \mu\text{m}$ by weathering (DePaolo et al., 2006). This is based on the *direct ejection* of ^{234}U (via the short-lived ^{234}Th) from detrital minerals following the alpha decay of ^{238}U (Kigoshi, 1971). Direct ejection leads to the formation of a ^{234}U -depleted rind on the surface of detrital grains (Fig. 1); however, this ^{234}U -depleted rind is only measureable in fine-grained particles ca. $<63\ \mu\text{m}$ due to their large surface-area-to-volume-ratio. Comminution ages (t) are calculated from the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the detrital minerals (A_{meas}), the initial activity ratio of parent material (assumed to be 1, A_0), the decay constant of ^{234}U (λ_{234}), and the *direct-recoil fraction* (f_a), which represents the number of ^{234}U nuclides directly-ejected out of the grain. The equation for calculating an age is shown in Equation 1 (DePaolo et al., 2006):

$$t = -\frac{1}{\lambda_{234}} \ln \left[\frac{A_{\text{meas}} - (1 - f_a)}{A_0 - (1 - f_a)} \right] \quad (1)$$

Thus far, the technique has been successfully applied to a North Atlantic marine core (DePaolo et al., 2006), palaeo-channel deposits in south-eastern Australia (Dosseto et al., 2010), and ice cores in Antarctica (Aciego et al., 2011). Lee et al. (2010) attempted to calibrate the calculation of the direct-recoil fraction by assuming the transport time of glacial sediment was negligible. The calculated ages were in reasonable agreement with the depositional age chronology, but further work is required to accurately constrain the direct-recoil fraction. Studies of palaeo-channels deposits in the Cooper Creek in central Australia (Handley et al., 2013a), and the alluvial deposits in the Flinders Ranges in South Australia (Handley et al., 2013b), found that many of the calculated comminution ages were less than the depositional age. This shows that comminution dating approach is currently only useful as a relative proxy for discerning between extreme variations in sediment transport (e.g. DePaolo et al., 2006; Dosseto et al., 2010) and measuring the release of ^{234}U from solids to the surrounding medium (e.g. Aciego et al., 2011; Bourdon et al., 2009). Further development is required to calculate reliable, absolute ages. Non-detrital matter such as carbonates, iron oxides, and organic matter, and clay minerals are ^{234}U -rich (Andersson et al., 2001; Andersson et al., 1998; Paces et al., 2013; Plater et al., 1992; Porcelli et al., 1997). The U isotope composition of these phases is not related to the ^{234}U -depletion in detrital minerals, which is due to the direct ejection of ^{234}U . Thus non-detrital matter must be completely removed in order for ages

calculated using the comminution dating technique to be reliable. Here we evaluate current sample pre-treatment procedures for removing non-detrital matter.

Sequential extraction procedures are currently used in comminution dating studies to remove non-detrital matter, and isolate the detrital minerals. It is difficult to compare results from different studies as each comminution dating study has used different sample pre-treatment methods: DePaolo et al. (2006) used a modified sequential extraction procedure based on Tessier et al. (1979), and a further 1.5 M HCl leach; Dosseto et al. (2010) removed organic matter by ashing at 550°C followed by a 1.5 M HCl leach; Lee et al. (2010) used a modified sequential extraction procedure based on Tessier et al. (1979); while Handley et al. (2013a; 2013b) used a modified sequential extraction procedure based on Schultz et al. (1998). Blanco et al. (2004) attempted to compare the extraction of U using Tessier et al. (1979) and Schultz et al. (1998); however, the overall extraction of U was similar and only the distribution of U in each fraction varied between the two procedures. Here we attempt to evaluate the removal of non-detrital matter using U isotopes in order to develop a standardised procedure for the comminution dating technique. Furthermore, we measure the surface area properties of the detrital minerals in order to assess the effect of sample pre-treatment on the resulting comminution ages.

2. Conceptual model

The alpha decay of ^{238}U results in three theoretical domains in soils and sediment, with distinct ($^{234}\text{U}/^{238}\text{U}$) activity ratios, as shown in Fig. 1.

Domain 1: ($^{234}\text{U}/^{238}\text{U}$) = 1

The inner-core of detrital minerals has the same isotopic composition of unweathered bedrock, and is in *secular equilibrium* whereby ($^{234}\text{U}/^{238}\text{U}$)_{S.E.} = 1. A system is in secular equilibrium if it has not undergone isotopic fractionation for at least four half-lives of the daughter nuclide. As the half-life of ^{234}U is $245,250 \pm 490$ a (Cheng et al., 2000), the inner-core of the detrital minerals will be in secular equilibrium if undisturbed for ca. 1 Ma (i.e. not exposed to weathering solutions).

Domain 2: ($^{234}\text{U}/^{238}\text{U}$) < 1

The outer ca. 50 nm ('outer-rind') of detrital minerals is ^{234}U -depleted due to the direct ejection of ^{234}U , which occurs on a length scale of ca. 30 nm in silicates (Hashimoto et al., 1985). Preferential leaching of ^{234}U from alpha-recoil tracks can also lead to ^{234}U -depletion by : i) the removal of embedded ^{234}U which is directly-ejected from adjacent grains (Fig. 1); and/ or ii) the exposure of recoil tracks to weathering solutions as a result of

mineral dissolution (Fleischer, 1980). This ^{234}U -depleted, outer-rind is only measureable in fine-grained detrital minerals (ca. $<63\ \mu\text{m}$) where the surface-area-to-volume ratio is large enough.

Domain 3: ($^{234}\text{U}/^{238}\text{U}$) > 1

Non-detrital matter consists of authigenic weathering products (e.g. organic matter, carbonates etc.) and clay minerals. Natural waters are enriched in ^{234}U due to alpha-recoil effects (Kigoshi, 1971). Thus non-detrital matter is generally ^{234}U -rich (Andersson et al., 1998; Plater et al., 1992). Furthermore, organic colloidal particles (e.g. humic compounds) have a high affinity for U and are also ^{234}U -rich (Andersson et al., 2001; Porcelli et al., 1997). Thus non-detrital matter generally has an activity ratio of ($^{234}\text{U}/^{238}\text{U}$) > 1.

Considering these three domains of ($^{234}\text{U}/^{238}\text{U}$) activity ratios, Lee (2009) suggested that the removal of non-detrital matter could be monitored by measuring the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue throughout a procedure. The removal of non-detrital matter should decrease the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue. The minimum ($^{234}\text{U}/^{238}\text{U}$) activity ratio should represent the optimal isolation of the detrital minerals. Any subsequent increase from this minimum value would imply dissolution of the ^{234}U -depleted outer-rind, and/ or readsorption of released ^{234}U (Fig. 2). An additional decrease in the ($^{234}\text{U}/^{238}\text{U}$) activity ratio following a sample pre-treatment procedure suggests that the removal of non-detrital matter was not complete.

In this study, firstly we monitored the ($^{234}\text{U}/^{238}\text{U}$) activity ratio by sampling an aliquot of the solid residue throughout a sequential extraction procedure. Repeat experiments were conducted to assess if the isotopic composition of the detrital minerals is consistent in separate sample aliquots. Mild HF etching was carried out to partially dissolve the outer-rind of the detrital minerals and determine the minimum ($^{234}\text{U}/^{238}\text{U}$) activity ratio. Finally, we evaluated the various sample pre-treatment procedures used in comminution age studies thus far using the ($^{234}\text{U}/^{238}\text{U}$) activity ratio.

3. Experimental methods and approach

A soil sample was collected from temperate rainforest on the Illawarra escarpment close to Otford, New South Wales, Australia (34.21°S 151.00°E 176m AMSL). The soil is a yellow podzol, which is developed over Triassic Sydney Basin Hawkesbury Sandstone (Young, 1982). The uppermost O-horizon was not sampled (0-0.1 m) and soil was collected from the A-horizon at a depth of 0.1-0.5 m. Suspended river sediment was sampled from the Leichardt River from the Gulf of Carpentaria drainage basin in northern Australia (Martin et al., 2014 in prep.), and marine sediment from core MD-32 in the corresponding Gulf of Carpentaria sedimentary

basin (Chivas et al., 2001). All samples were wet-sieved at 63 μm using deionised H_2O . The $<63 \mu\text{m}$ fraction was retained, dried in an oven at 50 $^{\circ}\text{C}$ and homogenised by gentle mixing with an agate mortar and pestle. Experiments were carried out with 2 g aliquots of dry, homogenised sample. An orbital shaker at 200 rpm was used to agitate samples for experiments at room temperature and experiments requiring higher temperatures were carried out on a hotplate, and shaken manually every hour. The solid and aqueous phases were separated by centrifugation at 7000 rpm for 10 minutes. The aqueous phase was removed using disposable Pasteur pipettes (previously-rinsed with 2 % HNO_3) and retained for later analysis. After each step, the solid residues were rinsed twice with 10 mL 18.2 M Ω H_2O before collecting 100 mg aliquots for later analysis. In Experiments 1, 2, and 4 the leached sediment was dried and weighed after each step to determine the mass of the material removed by each step of the procedures.

The following operationally-defined phases are removed in the sequential extraction procedure from Tessier et al. (1979) and Schultz et al. (1996) (herein referred to as Tessier's and Schultz' procedure, respectively): the *exchangeable fraction* (F1), which refers to elements adsorbed to mineral surfaces; the *acid-soluble fraction* (F2), which is dissolved by acidic solutions and targets carbonate minerals such as calcite and dolomite; the *reducible fraction* (F3), which targets iron and manganese oxides, hydroxides, and oxyhydroxides, with the use of a chemical reducing agent; and the *oxidisable fraction* (F4), which is removed by chemical or physical oxidation and targets organic matter. The remaining material following the removal of these operationally-defined fractions is referred to as the *residual fraction*, which should represent the detrital minerals. The reagents and conditions for each sequential extraction procedure are shown in Table 1.

In Exp. 1, the soil sample was leached according to Lee (2009), which utilises a modified version of Tessier's procedure (herein referred to as 'Lee's procedure'). In comparison to Tessier's procedure, Lee's procedure replaces MgCl_2 with 1 M $\text{Mg}(\text{NO}_3)_2$ for the removal of the exchangeable fraction. This is because the chloride ion has been shown to remove non-detrital matter from other phases (Leleyter and Probst, 1999).

In Exp. 2, we tested how the addition of sodium citrate to reagent solutions affects U removal in sequential extraction procedures. Extraction solutions are expected to be ^{234}U -rich and thus readsorption of U should be minimised. Sodium citrate has been shown to be the most effective complexing agent for U (Lozano et al., 2011). In Exp. 2, the same reagents and conditions were used as Exp. 1, except for the addition of 10 mg of sodium citrate per gram of sample to the reagent solution at the start of each reaction.

In Exp. **3**, following sequential extraction, mild HF/ HCl etching was carried out at room temperature using 20 mL 0.3 M HF/ 0.1 M HCl per gram of sample. This was carried out in order to partially dissolve the outer-rind of detrital minerals, increase the ($^{234}\text{U}/^{238}\text{U}$) activity ratio and find the minimum activity ratio (Fig. 2). Sodium citrate was added to the solution using 10 mg of sodium citrate per gram of sample. A solution of 0.3 M HF/ 0.1 M HCl was chosen as mild HCl can remove any other non-detrital matter remaining following sequential extraction (Sutherland, 2002). The soil sample used in Exp. **3** was initially leached using the sequential extraction procedure in Exp. **1**. During mild HF/ HCl etching, aliquots of the solid residue and aqueous solution were taken at 0, 2, 4 and 8, and 24 h. In Exp. **3**, the river sediment, marine sediment and rock standard BCR-2 were also leached using the mild HF/ HCl etching procedure. Shorter reaction times (<6 h) than for the soil sample were chosen as our results showed that prolonged periods of etching (24 h) did not change the ($^{234}\text{U}/^{238}\text{U}$) activity ratio.

In Exp. **4**, the soil sample was leached using Schultz' procedure (Table 1). In Experiments **5** and **6**, we tested the removal of non-detrital matter using other procedures which have been used in comminution age studies. In Exp. **5**, the soil sample was leached by ashing in a furnace at 550°C as recommended by Heiri et al. (2001) and then leached using 16 mL $\text{Mg}(\text{NO}_3)_2$ at room temperature for 50 mins, as recommended by Lee (2009). In Exp. **6**, the soil sample was leached by single-acid-extraction using 40 mL of 0.5 M HCl at room temperature for 1 h, as recommended by Sutherland et al. (2002). In Exp. **7**, the soil sample was initially leached using the procedure in Exp. **1** and then leached sequentially by the following procedures: i) ashing in a furnace and rinsed with 16 mL $\text{Mg}(\text{NO}_3)_2$ at room temperature for 50 mins; ii) 40 mL of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ / AcOH at pH 2, and 96°C for 5 h; and iii) 40 mL of 0.5 M HCl at room temperature for 1 h.

X-ray diffraction analysis was carried out to assess if changes in the activity ratio are a result of the preferential dissolution of clay minerals, and the particle size distribution was measured in order to monitor changes in the particle size. It is important to understand how sample pre-treatment procedures affect not only the ($^{234}\text{U}/^{238}\text{U}$) activity ratio, but also the surface area properties. Thus the Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) and fractal dimension were measured. Ages were calculated using the fractal direct-recoil model presented in Bourdon et al. (2009). This takes into account the BET specific surface area (S_{BET}), density of solid phase (ρ), recoil length using a value of 30 nm for ^{234}Th (Hashimoto et al., 1985) (R), the fractal dimension (D), and diameter of the adsorbate gas (a), as shown in Equation 2:

$$f_{\alpha} = \frac{1}{4} S_{\text{BET}} \rho R \left[\frac{2^{D-1}}{4-D} \left(\frac{a}{R} \right)^{D-2} \right] \quad (2)$$

The C constant was also calculated from the BET equation, which provides information on the interaction between the adsorbate (N_2) and the mineral surface. As N_2 has a molecular quadrupolar moment (Buckingham et al., 1968), it is energetically favourable for N_2 to adsorb on polar surfaces, such as silicate minerals, which leads to a higher C constant. Adsorption onto non-polar surfaces, such as organic matter results in a lower C constant (Mayer, 1994). The C constant is also related to the extent of microporosity; a higher C constant indicates a greater degree of microporosity (Hudec, 2008).

4. Analytical techniques

The chemicals used in sequential extraction procedures were as follows (grade and supplier shown in brackets, respectively): glacial AcOH (Reagent grade, ThermoFisher), NH_4OAc (TraceSELECT>99.9999%, Sigma-Aldrich), $NH_2.OH.HCl$ (TraceSELECT>99.9999%, Sigma-Aldrich), HF 32 % (Suprapur, Merck), H_2O_2 30 % (Reagent grade, Merck), $Mg(NO_3)_2$ (Suprapur, Merck), HNO_3 69 % (ACS Reagent, Merck), NaOAc (Analytical reagent, Merck), Na(citrate) (Analytical reagent, Sigma-Aldrich) and NaOCl 5-6 % (Analytical reagent, Sigma-Aldrich). In all experiments, 18.2 M Ω H_2O from a Milli-Q® Gradient A10® filtration system was used.

Strong acid dissolution of solid residues were carried out at Wollongong Isotope Geochronology Laboratory, University of Wollongong. Prior to dissolution, ca. 100 mg of material was weighed and a known amount of $^{229}Th-^{236}U$ tracer was added. Samples were dissolved in a solution of 2.5 mL 32 % HF and 0.5 mL 69 % HNO_3 , heated overnight at 100°C, and dried to incipient dryness. Following this, 3 mL of 32 % HCl was added and where necessary, H_3BO_3 was added to dissolve fluorides. The samples were heated overnight at 80°C and dried to incipient dryness. Following this, 0.5 mL 69 % HNO_3 was added, dried at 100°C to incipient dryness and this step was repeated twice. For isotopic measurements, 2 mL of 1.5 M HNO_3 was added following dissolution and the solutions were sonicated for 15 min, and heated at 100°C, to ensure re-dissolution. For isotopic measurements, U was separated by standard chromatographic techniques using a TRU resin (Eichrom) as described in Luo et al. (1997). The $^{234}U/^{238}U$ ratios were measured using 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 cup yield were corrected by standard bracketing using synthetic standard U010 and the accuracy of standard bracketing was checked using U005A. Accuracy was assessed by analysing a rock standard (BCR-2, U.S. Geological Survey) known to be in secular equilibrium whereby $(^{234}U/^{238}U)_{S.E.} = 1$. For isotopic dilution measurements, the $(^{236}U/^{238}U)$ activity ratio was tail corrected by measuring the intensity at 235.5 and 236.5 amu. The measured $(^{234}U/^{238}U)$ activity ratios were within 0.7 %

of this value (0.998 ± 0.003 and 1.007 ± 0.004). The measured U concentrations were 1.70 ± 0.01 and 1.73 ± 0.01 ppm which are all within error of the value recommended (Wilson, 1997).

For acid digestion and column chromatography, the following chemicals were used: HCl 32 % (Suprapur, Merck), HF 32 % (Suprapur, Merck) and HNO₃ 69 % (Suprapur, Merck). All dilutions were made using 18.2 MΩ H₂O from a Milli-Q® Gradient A10® filtration system.

For sequential extraction solutions, U concentrations were determined by dilution and using calibration curves of known concentration. The U concentrations were not determined by isotopic dilution due to difficulties in separating U from sequential extraction reagents with high cation concentrations. Solutions were diluted in 2 % v/v HNO₃ to ensure major ion concentrations reagents in solutions were <1 ppm, with the following dilutions factors: 48600 for Mg(NO₃)₂, 92000 for NaOAc/ AcOH, 14200 for NH₂OH.HCl/AcOH, 405 for H₂O₂, 60600 for NH₄OAc, 625 for 0.3 M HF/ 0.1 M HCl etching solutions, and 7500 for NaOCl. Concentrations were analysed on an Agilent 7500 Series Inductively-Coupled Plasma Mass Spectrometer at UOW and calculated quantitatively by constructing a calibrations curve using 6 standards with U concentrations ranging from 0 to 100 ppb. Total procedure blanks were ≤ 34 pg for U.

For X-ray diffraction measurements, samples were crushed to <4 mm with a Tollmill crusher (TEMA). The samples were then mounted in aluminium holders and placed in a Phillips 1130/90 diffractometer with Spellman DF3 generator set to 1 kW. They were loaded and analysed through an automatic sample holder. The 1 kW energy is achieved by setting the diffractometer to 35 kV and 28.8 mA. Samples were analysed between 4 and 70° 2-theta at 2° per minute with a step size of 0.02. Traces were produced through a GBC 122 control system and analysed using Traces, UPDSM and SIROQUANT softwares. Error was assessed by the chi-squared (χ^2) value which compares the observed data (measured XRD spectrum) with expected data (hypothetical XRD spectrum according to user-selected minerals). Particle size distributions were measured by laser diffraction using a Malvern Mastersizer 2000 particle size analyser by dispersing a few mg of sample in H₂O. Surface area measurements were determined by N₂ gas adsorption using a Quantachrome iQ surface area analyser. Samples were degassed for 3 h at 200 °C. The specific surface area (S_{BET}) was determined using 5-7 adsorption points from the partial pressure (P/P_0) range 0.05-0.30 and adjusted for the best fit of the Multi-point BET equation ($R^2 > 0.9999$). The fractal dimension was determined using the Neimark-Kiselev Method (Neimark, 1990).

5. Results

5.1. Uranium isotope and concentration measurements

Heterogeneity is observed for the ($^{234}\text{U}/^{238}\text{U}$) activity ratio and U concentration of the <63 μm fraction of the untreated soil (Table 2).

In Exp. 1, sequential extraction was carried out using Lee's procedure. The ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue decreased stepwise following removal of each fraction (except the acid soluble fraction), to a final value of 0.939 ± 0.003 . The final activity ratio of a repeat experiment was within analytical error (Fig. 3A). A total of 32 ± 2 wt. % of U was extracted and the majority of U was found in the reducible and oxidisable fractions (Fig. 3B). In Exp. 2, sequential extraction was carried out using Lee's procedure with sodium citrate added to each reagent as a complexing agent. The ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue decreased sequentially following removal of each fraction to 0.938 ± 0.005 and the final activity ratio of a repeat experiment was within analytical error (Fig. 3A). In Exp. 2, the percentage of U extracted increased by 47 %, compared to Exp. 1. The majority of U was extracted in the acid-soluble, reducible and oxidisable fractions (Fig. 3B).

In Exp. 3, the ($^{234}\text{U}/^{238}\text{U}$) activity ratio decreased from 0.939 ± 0.003 following sequential extraction to a minimum of 0.917 ± 0.003 after 4 h of mild HF/ HCl etching (Fig. 4A). Mild HF/ HCl etching extracted a further 6 ± 0 wt. % of U after 24 h (Fig. 4B). In Exp. 3, the mild HF/ HCl etching procedures was also tested on river and marine sediments. The minimum ($^{234}\text{U}/^{238}\text{U}$) activity ratio was found after sequential extraction and 2 h of etching for both the river and marine sediments (Fig. 4A). Sequential extraction and 4 h of mild HF/ HCl etching procedure on rock standard BCR-2 decreased the ($^{234}\text{U}/^{238}\text{U}$) activity ratio to 0.992 ± 0.002 (Fig. 4A).

In Exp. 4, the final activity ratio following sequential extraction using Schultz' procedure was 0.927 ± 0.003 , which is lower than the final activity ratios in Exp. 1 and 2 (Fig. 3A). The majority of U was extracted in the oxidisable fraction (Fig. 3B). In Exp. 5, the final activity ratio following ashing at 550°C and a 1 M $\text{Mg}(\text{NO}_3)_2$ rinse was 0.974 ± 0.002 . In Exp. 6, the final activity ratio following single-acid extraction using 0.5 M HCl was 0.969 ± 0.002 . In Exp. 7, additional leaching experiments were carried out sequentially following sequential extraction in Exp. 1. The activity ratio decreased from 0.939 ± 0.005 to 0.936 ± 0.002 following additional ashing and a $\text{Mg}(\text{NO}_3)_2$ rinse, and to 0.933 ± 0.002 following an additional $\text{NH}_2\text{OH}.\text{HCl}$ leach. The activity ratio then remained within analytical error following single-acid extraction using 0.5 M HCl. A summary of the activity ratios following experiments with the soil sample is shown in Table 3.

5.2. Physical Analyses

Sequential extraction procedures resulted in a total loss of ca. 100 mg g⁻¹ of sample (Table 4). In each experiment, the removal of the exchangeable fraction did not result in significant mass loss (< 2 mg g⁻¹). In Exp. 1 and 4, the majority of mass was removed in the reducible fraction and in Exp. 2, the majority of mass was removed in the oxidisable fraction. The variability in the proportion of mass removed in Exp. 1 and 2 indicate that the removal of mass is highly variable.

In Exp. 1, sequential extraction decreased the relative volume of particles <10 µm and concurrently decreased particles >10 µm (Fig. 5). In contrast, in Exp. 3, mild HF/ HCl etching following sequential extraction decreased the relative volume of particles <10 µm and increased particles >10 µm (Fig. 5).

The mineralogy of the soil sample was determined before and after sequential extraction in Exp. 1 by X-ray diffraction. The mineralogy of the <63 µm fraction of the untreated soil is mainly quartz (72 %), kaolinite (11 %) with small amounts (<5 %) of illite, muscovite, zircon, magnetite, chlorite, ilmenite and rutile ($\chi^2 = 3.2$). These results are consistent with the quartzose sandstone lithology from which the soil is derived. The mineralogy remained unchanged following sequential extraction in Exp. 1 ($\chi^2 = 8.58$): quartz (74 %), and kaolinite (8 %) and small amounts (<6 %) of illite, muscovite zircon, magnetite, chlorite, ilmenite and rutile.

The effect of sample pre-treatment on the surface area properties were tested on the soil sample (Table 5). Sequential extraction increased S_{BET} in both Exp. 1 and 4. In Exp. 3, mild HF/ HCl etching initially increased S_{BET} following 4 h of etching and subsequently decreased following 24 h of etching. The fractal dimension of the soil remained unchanged following Lee's procedure in Exp. 1, but decreased following Schultz' procedure in Exp. 4. In Exp. 3, mild HF/ HCl etching decreased the fractal dimension. Sequential extraction increased the C constant in Exp. 1 and 4. In Exp. 3, mild HF/ HCl etching initially decreased the C constant following 4 h of etching, and then increased following 24 h of etching.

6. Discussion

6.1. Validation of the methodology

Lee (2009) proposed that the removal of non-detrital matter from fine-grained soils and sediment ($<63\ \mu\text{m}$) can be monitored by measuring the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue (Fig. 2). We tested this by measuring the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue throughout sequential extraction procedures, and observed the sequential decrease of the activity ratio in Experiments 1 and 2 (Fig. 3A). X-ray diffraction measurements showed that the decrease in the ($^{234}\text{U}/^{238}\text{U}$) activity ratio cannot be attributed to the preferential dissolution of ^{234}U -rich clay minerals. Furthermore, particle size distribution measurements also showed that there is a relative increase in particles $<10\ \mu\text{m}$ (Fig. 5), which suggests that the dissolution of clay minerals is minimal. The increase in particles $<10\ \mu\text{m}$ following sequential extraction is attributed to the break-up of large aggregates which are cemented by organic and inorganic coatings (Horowitz and Elrick, 1987). Alternatively, the preferential leaching of ^{234}U from damaged lattice sites could decrease the activity ratio; however, tests on rock standards known to be in secular equilibrium have shown that sequential extraction procedures do not induce preferential leaching (Suresh et al., 2014). Thus the decrease of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio throughout sequential extraction is attributed to the removal of authigenic weathering products and organic matter.

Heterogeneity is observed in U concentrations and ($^{234}\text{U}/^{238}\text{U}$) activity ratios in the 3 aliquots of the untreated soil samples (Table 2). We attribute this to variable amounts of non-detrital matter in the different aliquots. It is difficult to avoid such heterogeneity as grinding would affect S_{BET} and the resulting comminution age calculations. Furthermore, grinding would create fresh mineral surfaces, which would alter mineral reactivity with reagents. Despite this, the final ($^{234}\text{U}/^{238}\text{U}$) activity ratios were remarkably similar between replicates and different experiments following sequential extraction (Fig. 3A, Table 3). Firstly, this suggests that despite variations in the amount of U removed in each operationally-defined fraction using Lee's and Schultz' procedures (Fig. 3B), the overall removal of U is consistent, as observed in Blanco et al. (2004). Secondly, and importantly, the U isotope composition of the detrital minerals following sequential extraction appears to be homogeneous.

6.2. The addition of a complexing agent

Readsorption of U during sequential extraction procedures could artificially increase the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the detrital minerals. The addition of sodium citrate as a complexing agent increased the percentage of U extracted in the exchangeable and acid-soluble fraction (Exp. 2, Fig. 3B). The percentage of U extracted in the

exchangeable fraction with the addition of sodium citrate is high in comparison to other studies (6.5 wt. %), which report <1 wt. % of U extracted (Aubert et al., 2004; Virtanen et al., 2013). This suggests that either: i) sodium citrate is extracting U from other non-detrital phases; or ii) the proportion of U extracted in the exchangeable fraction in other studies has been consistently underestimated due to the readsorption. The increased extraction of U from the exchangeable fraction does not affect the ($^{234}\text{U}/^{238}\text{U}$) activity ratio, which suggests that this material has a similar activity ratio to the untreated soil. The extraction of U in the acid-soluble fraction increases over fourfold following the addition of sodium citrate to sequential extraction reagents (Fig. 3B). It should be noted that the increased extraction of U in the acid-soluble fraction could be due to a greater initial amount of carbonates in the soil aliquot used. This is evidenced by the higher ($^{234}\text{U}/^{238}\text{U}$) activity ratio following removal of the exchangeable fraction in Exp. 2. However, the ($^{234}\text{U}/^{238}\text{U}$) activity ratio decreased in Exp. 2, whereas the activity ratio remained within analytical error without the addition of sodium citrate in Exp. 1 (Fig. 3A). This suggests U is readsorbed without the addition of a complexing agent. The final activity ratio following sequential extraction with, and without the addition of sodium citrate were within analytical error (Fig. 3A). This suggests that U readsorbed during the removal of the acid-soluble fraction is removed later in the procedure.

6.3. Mild HF/ HCl etching procedure

To assess whether the removal of non-detrital matter following sequential extraction is complete, a previously-leached sample was etched using a solution of 0.3 M HF/ 0.1 M HCl following sequential extraction. Mild HF/ HCl etching further decreased the ($^{234}\text{U}/^{238}\text{U}$) activity ratio and the minimum was found following 4 h of etching. This decrease in the activity ratio indicates that the removal of non-detrital matter by sequential extraction was incomplete (Fig. 2). Particle size distribution measurements revealed a relative decrease in particles <10 μm following a prolonged duration of etching. This suggests that the decrease in the activity ratio can at least partly be attributed to the dissolution of ^{234}U -rich clay minerals. As the U isotope composition of clay minerals is not related to the direct ejection of ^{234}U , they should be removed from samples for the comminution dating technique.

Mild HF/ HCl etching decreased ($^{234}\text{U}/^{238}\text{U}$) activity ratio also of the river sediment, marine sediments, and rock standard. The ($^{234}\text{U}/^{238}\text{U}$) activity ratio of rock standard BCR-2 following 4 h of etching decreased to 0.992 ± 0.002 . This indicates that mild HF/ HCl etching results in some preferential leaching of ^{234}U (Fig. 1). As rock standards represent freshly-crushed rock, which have large amounts of fresh surface area, our experiment

likely overestimates the preferential leaching of ^{234}U . Freshly-exposed surfaces contain labile ^{234}U , which are easily removed by weathering solutions, and leaching experiments suggest that they are removed in the natural environment within ca. 200 a (Fleischer, 1980). As it is likely that this fraction of labile ^{234}U would be instantly lost on the geological timescale, the comminution age technique must attempt to take preferential leaching into account in order to calculate reliable ages.

In addition to the preferential leaching of ^{234}U and the dissolution of clay minerals, it is also possible that mild HF/HCl etching also removes refractory non-detrital matter. Other studies observe that a proportion of organic matter is refractory, resistant to ashing and chemical oxidation procedures, and is only removable by HF treatment (Kaiser and Guggenberger, 2003; Kleber et al., 2005; Mayer, 1994; Mikutta et al., 2006; Outola et al., 2009). The resistant nature of this refractory organic matter is due to: i) micropores limiting diffusion of solutions into pores (Mikutta and Mikutta, 2006); ii) reactive hydroxyl groups on mineral surfaces stabilising organic matter (Mikutta et al., 2006); iii) chemical oxidation by H_2O_2 forming more resistant phases (Mikutta et al., 2005).

6.4. Evaluation of other procedures

The effectiveness of sample pre-treatment procedures used in comminution studies was assessed using U isotopes. The greatest decrease of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio, and the highest percentage of U extracted, was observed Exp. 4 using procedure from Schultz et al. (1998). This is attributed to the increased effectiveness of NaOCl for removing the oxidisable fraction in comparison to H_2O_2 , which has also been shown elsewhere (Mikutta et al., 2005).

Ashing followed by a $\text{Mg}(\text{NO}_3)_2$ rinse decreased the activity ratio and appears to effectively remove the oxidisable fraction (Exp. 5, Table 3). Lee (2009) found that removal of the oxidisable fraction using H_2O_2 and ashing were similarly effective. However, the most effective method of removing organic matter appears to be using NaOCl.

The decrease in the ($^{234}\text{U}/^{238}\text{U}$) activity ratio following removal of the acid-soluble fraction using 0.5 M HCl is similar to the decrease using NaOAc/ AcOH and sodium citrate. However, the decrease in the activity ratio following single-acid extraction is greater than using NaOAc/AcOH without sodium citrate (Exp. 2). This is further proof for the readsorption of U occurs with NaOAc/AcOH and no complexing agent. The much higher reagent-volume-to-sample ratio in single-acid extraction, compared to the NaOAc/ AcOH solution likely

inhibits the readsorption of U (20 vs. 8 mL g⁻¹). These results are in contrast to Lee (2009) who found that single-acid extraction of alluvial sediment, under the same reactions conditions, increased the (²³⁴U/²³⁸U) activity ratio. This was attributed to the dissolution of the ²³⁴U-depleted, outer-rind of the detrital minerals due an insignificant amount of non-detrital matter present.

A previously-leached sample was subject to further leaching to determine the nature of the residual non-detrital matter following sequential extraction. The (²³⁴U/²³⁸U) activity ratio is unchanged following ashing and a Mg(NO₃)₂ leach, and decreased following an additional NH₂OH.HCl/ AcOH leach (Exp. 7, Table 3). This indicates that a proportion of the non-detrital matter remaining after sequential extraction is reducible and could be the result of either: i) incomplete removal of Fe/ Mn oxides during sequential extraction; or ii) the stabilisation of poorly-crystalline material during H₂O₂ oxidation (Mikutta et al., 2005).

6.5. The effect of sequential extraction and etching procedures on the surface properties of soil

The effect of sample pre-treatment on the surface area properties of the soil was assessed. Sequential extraction increases S_{BET} of the soil sample (Exp. 1 and 4, Table 5), which is explained by increased pore space availability following removal of non-detrital matter, and is referred to as *occluded surface area* (Kaiser and Guggenberger, 2003; Mayer, 1994). This suggests that the majority of non-detrital matter removed during sequential extraction is comprised low surface area material, such as organic matter. Initially, S_{BET} increased following sequential extraction short durations of mild HF/ HCl etching and then decreased following a longer duration of etching (Exp. 3, Table 5). This suggests that mild HF/ HCl etching initially removes low surface area material, such as organic matter, which is followed by the removal of high surface area material, such as clay minerals.

Sequential extraction increased the C constant (Exp. 1 and 4, Table 5), which suggests that the coverage of the surface of silicate minerals by organic matter is decreased (Mayer, 1994). The C constant initially decreased following sequential extraction and short durations of mild HF/HCl, and then increased following a longer duration of etching. This suggests that polar material and/or micropores are initially removed during and long durations remove non-polar material such as organic matter.

The fractal dimension remained constant following sequential extraction in Exp. 1, and decreased following mild HF/ HCl etching and sequential extraction in Exp. 4 (Table 5). Fractal behaviour in sediment is attributed to the presence of clay minerals, and authigenic weathering products (Krohn, 1988a; Krohn, 1988b; Wong et al.,

1986). The development of porosity of minerals has also been shown to exhibit fractal behaviour (Katz and Thompson, 1985). The lack of decrease in the fractal dimension following sequential extraction indicates that the removal of non-detrital matter in Exp. 1 is incomplete. Alternatively, the increased porosity available to N₂ following the removal of non-detrital matter could be limiting the observed decrease in the fractal dimension. The decrease in the fractal dimension following mild HF/ HCl etching indicates the removal of non-detrital matter and/or clay minerals.

Sequential extraction using the procedure from Schultz et al. (1998) leads to the highest S_{BET} and C constant, and lowest fractal dimension (Exp. 4, Table 5). These results indicate that this procedure represents the optimal balance between preserving the surface morphology of detrital minerals, and removing non-detrital matter.

6.6. Calculated ages

The ages inferred by the comminution dating approach are strongly dependent on the surface area properties of the detrital minerals. Here, we show the effect of sample pre-treatment on the calculated age using the fractal direct-recoil model. The inferred ages are generally >1000 ka, which is beyond the limit of the technique (Table 6). However, it is unlikely that the activity ratio of the starting material is 1 due to the preferential leaching of ²³⁴U (as discussed in Section 6.3). Using the activity ratio of the rock standard following sequential leaching and mild HF/ HCl etching as the initial activity ratio (0.992), the ages are still beyond the limit of the technique. Assuming a hypothetical initial activity ratio of 0.95 is required for the ages to become ‘reasonable’ i.e. within the limit of the technique. The ages of samples using different sequential extraction procedures are with error of each other (Exp. 1 and 4, Table 6). Mild HF/ HCl etching following sequential extraction leads to much older ages, which is due to: i) further removal of ²³⁴U-rich non-detrital matter; and ii) lower S_{BET} following the removal of high surface area clays minerals. The presence of clay minerals will lead to artificially low ages and may explain why inferred comminution ages from Handley et al. (2013b) for clay-rich sediment from the Flinders Ranges in South Australia were much lower than the depositional ages.

Conclusion

Sequential extraction resulted in a stepwise decrease of the (²³⁴U/²³⁸U) activity ratio of the solid residue following the removal of the operationally-defined, non-detrital phases. X-ray diffraction and particle size distribution measurements revealed that this decrease of the activity ratio during sequential extraction is due to the removal of authigenic weathering products and organic matter. These results validate the proposal by Lee (2009) that the removal of non-detrital matter can be monitored by measuring the (²³⁴U/²³⁸U) activity ratio of the

solid residue (<63 μm fraction). Despite heterogeneous amounts of U in untreated soil aliquots, the activity ratios of samples following replicate sequential extraction experiments are similar. This suggests that the removal of non-detrital matter by sequential extraction procedures is consistent. Furthermore, this also suggests that the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the detrital minerals is homogeneous following sequential extraction.

The addition of a complexing agent (sodium citrate) to the sequential extraction reagents increased the percentage of U extracted in the exchangeable and acid-soluble fraction. However, this did not affect the final ($^{234}\text{U}/^{238}\text{U}$) activity ratio at the end of the procedure. This suggests that readsorbed U is removed later in the procedure. The addition of sodium citrate to sequential extraction reagents increases the overall extraction of U, and is thus recommended.

Mild HF/ HCl etching further decreased the ($^{234}\text{U}/^{238}\text{U}$) activity ratio following sequential extraction, and this was also observed for river and marine sediments. Particle size distribution measurements show a relative decrease in particles <10 μm , which suggests that mild HF/HCl etching likely dissolves clay minerals. The U isotope and surface area composition of clay minerals are not related to the loss of ^{234}U by direct ejection, and thus should be removed for the comminution dating technique. Mild HF/ HCl etching following sequential extraction on a rock standard revealed a small amount of preferential leaching of ^{234}U (<1 %). However, this likely represents a maximum loss of ^{234}U as rock standards are comprised crushed rock. In any case, the preferential leaching of ^{234}U likely occurs in most weathering environments, and further development of the comminution dating technique must account for this. Efforts must be made to quantify the loss of labile ^{234}U , which could be achieved with mild HF/ HCl etching experiments. Although mild HF/ HCl etching may induce a small amount of preferential leaching, mild HF/ HCl etching following sequential extraction is recommended.

Evaluation of current sample pre-treatment methods in terms of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio reveals that the sequential extraction procedure from Schultz et al. (1998) is the most effective. This is attributed to NaOCl removing the oxidisable fraction more efficiently than H_2O_2 , which has also been shown in other studies. Further work should therefore involve testing the mild HF/ HCl etching procedure with Schultz' procedure.

Sequential extraction increased the specific surface area (S_{BET}), which is attributed to the increased porosity following the removal of non-detrital matter from the detrital minerals. Furthermore, sequential extraction increased the C constant suggesting a decreased coverage of detrital minerals by organic matter. The fractal dimension was unchanged following sequential extraction using Lee's procedure, but decreased using Schultz' procedure. As non-detrital matter is expected to have a high fractal dimension, this suggests the latter procedure

removes non-detrital matter more effectively. Mild HF/HCl resulted in an initial increase in S_{BET} and subsequent decrease which is attributed to the removal of non-detrital matter and then clay minerals. The fractal dimension also decreases following etching, which suggests further removal of non-detrital matter and clay minerals.

The majority of inferred ages are beyond the limit of the technique (1000 ka). Assuming an initial ($^{234}\text{U}/^{238}\text{U}$) activity ratio of 0.95 is required for ages to be within the limit of the technique, which is much lower than the ^{234}U -depletion observed in the rock standard following mild HF/HCl etching and sequential leaching. Inferred ages are within analytical error following different sequential extraction procedures. Mild HF/ HCl etching following sequential extractions leads to much older ages, which is attributed to the lower activity ratio and surface area following the removal of non-detrital matter. These results explain why comminution ages less than the depositional age have been inferred in some studies. Further work should involve testing the different sample pre-treatment procedures on a sample dated by other geochronological methods, similar to the approach by Lee et al. (2010) for refining calculation of the direct-recoil fraction.

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Tables

Table 1. Reagents and conditions used in the sequential extraction procedures developed by Tessier et al. (1979) and Schultz et al. (1998).

Target phase	Reagents and Conditions	
	Tessier et al. (1979) ^a	Schultz et al. (1998) ^{a,b}
Water-soluble	8 mL H ₂ O	20 mL H ₂ O
(F0)	Room temp./1 h	Overnight
Exchangeable	8 mL 1 M MgCl ₂ at pH 7	20 mL 0.4M MgCl ₂ at pH 5
(F1)	Room temp./ 1 h	Room temp./1 h
Acid-soluble	8 mL NaOAc/ AcOH at pH 5	20 mL 1M NaOAc/ AcOH at pH 4
(F2)	Room temp./ 6 h	Room temp./ 2 h*
Reducible	20 mL 0.04 M NH ₂ OH.HCl/ AcOH at pH 2	20 mL 0.04 M NH ₂ OH.HCl/ AcOH at pH 2
(F3)	96 °C/ 5 h	Room temp./ 5 h
Oxidisable	8 mL 0.02M HNO ₃ / H ₂ O ₂ at pH 2	
	85°C/ 2 h	
	3 mL H ₂ O ₂ at pH 2	20 mL NaOCl at pH 7.5
	85 °C/ 3h	96 °C/ 0.5 h*
	5 mL 3.2M NH ₄ OAc in HNO ₃ 20% diluted to	
	20 mL with H ₂ O	
(F4)	Room temp./ 30 min	

^aReagent volumes for 1 g of sample.

^bThe order of extraction modified so that the oxidisable (F4) fraction is removed before F2 and F3.

*Extractions repeated twice.

625 **Table 2. (²³⁴U/²³⁸U) activity ratio, and U concentration of the untreated soil (< 63 μm fraction)**

Sample	(²³⁴ U/ ²³⁸ U)	U (ppm)
A	0.993 ± 0.002	2.7 ± 0.1
B	1.080 ± 0.001	2.4 ± 0.1
C	0.996 ± 0.002	3.2 ± 0.1
Average ^a	1.019 ± 0.002	2.6 ± 0.1

626 A, B and C represent dissolution of separate aliquots and error shown represents 2σ internal standard error.

627 ^aWeighted average value (2σ, n = 3)

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Table 3. ($^{234}\text{U}/^{238}\text{U}$) activity ratios and the cumulative percentage of U extracted (relative to the amount of U in the untreated soil) in Experiments 1-7.

Experiment	Experiment summary	Fractions removed	($^{234}\text{U}/^{238}\text{U}$)	U (wt. %)
1	Sequential extraction procedure from Lee (2009)	F1	0.990 ± 0.003	0.27 ± 0.18
		F1, F2	0.996 ± 0.003	4.4 ± 0.7
		F1, F2, F3	0.961 ± 0.003	19 ± 1
		F1, F2, F3 and F4	0.939 ± 0.003	32 ± 2
		F1, F2, F3 and F4 (replicate)	0.935 ± 0.003	n/a
2	Sequential extraction procedure from Lee (2009) + sodium citrate	F1	1.007 ± 0.003	6.5 ± 0.6
		F1, F2	0.971 ± 0.003	24 ± 2
		F1, F2, F3	0.963 ± 0.003	35 ± 2
		F1, F2, F3 and F4	0.938 ± 0.005	47 ± 2
		F1, F2, F3 and F4 (replicate)	0.931 ± 0.003	n/a
3 (0 h)	Sequential extraction procedure from Lee (2009) + mild HF/ HCl etch	F1, F2, F3, F4	0.939 ± 0.003	32 ± 2
3 (1 h)			0.930 ± 0.007	34 ± 2
3 (2 h)			0.923 ± 0.003	34 ± 2
3 (4 h)		F1, F2, F3, F4 and F5	0.917 ± 0.003	35 ± 2
3 (8 h)			0.919 ± 0.003	37 ± 2
3 (24 h)			0.923 ± 0.004	38 ± 2
4	Sequential extraction procedure from Schultz et al. (1998)	F1, F2, F3 and F4	0.927 ± 0.003	55 ± 3
5	Ashing and MgNO_3 rinse	F4	0.974 ± 0.002	n/a
6	0.5 M HCl	F2	0.969 ± 0.002	n/a
7	Additional leaching experiments following sequential extraction	F1	0.936 ± 0.002	n/a
		F1 and F3	0.933 ± 0.002	n/a
		F1, F3 and F2	0.933 ± 0.002	n/a

Experiments were conducted on the soil sample and the operationally-defined fractions are defined: exchangeable (F1), acid-soluble (F2), reducible (F3), oxidisable (F4) and refractory (F5). Error shown represents 2σ internal standard error. Values in brackets for Exp. **3** represent duration of mild HF/ HCl etching.

634 **Table 4. The amount of mass removed per gram of soil in Experiments 1, 2, 4, and 5.**

Fraction	Exp. 1	Exp. 2	Exp. 4	Exp. 5
	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)
F1	1.1	0.40	1.9	n/a
F2	7.0	20	11	n/a
F3	60	31	70	n/a
F4	41	32	13	64
Total	110	83	96	64

635 Operationally-defined fractions are defined: exchangeable (F1), acid-soluble (F2), reducible (F3), oxidisable (F4) and refractory (F5).

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Table 5. Particle size and surface area properties of the <63 μm fraction of the untreated soil sample, and following Experiments 1, 3 and 4.

Experiment	Mean diameter (μm)	S_{BET} (m^2g^{-1})	D	$\frac{C_{39}}{\text{constant}}$
Untreated	5.9	16	2.70	96
1	4.8	21	2.70	110
2	5.1	n/a	n/a	n/a
3 (4 h)	n/a	23	2.57	86
3 (24 h)	3.4	14	2.57	130
4	n/a	27	2.52	140
Estimated uncertainty	n/a	$\pm 0 \%$	$\pm 4.86 \%$	$\pm 3 \%$

Estimated uncertainty calculated from 2σ external standard error of replicate analyses. S_{BET} represents the specific surface area, and D represents the fractal dimension. Numbers in brackets for Exp. 3 represent the duration of etching.

643 **Table 6. Comminution ages calculated following the various sample pre-treatment procedures.**

Exp.	$(^{234}\text{U}/^{238}\text{U})$	f_a	t (ka)	t (ka)	t (ka)
			($A_0 = 1$) ^a	($A_0 = 0.99$) ^a	($A_0 = 0.95$) ^a
1	0.939	0.043	>1,000	>1,000	330
	± 0.003				± 57
3 (4 h)	0.917	0.069	>1,000	>1,000	>1000
	± 0.003				
3 (24 h)	0.923	0.042	>1,000	>1,000	520
	± 0.004				± 36
4	0.927	0.094	530	490	260
	± 0.003		± 46	± 46	± 46

644 ^aInitial ($^{234}\text{U}/^{238}\text{U}$) activity ratio (A_0)

645

Figure Captions

Figure 1. The three domains present in soils and sediment in terms of their respective ($^{234}\text{U}/^{238}\text{U}$) activity ratios and the two scenarios for ^{234}U -depletion: 1) direct ejection of ^{234}U (via the short-lived ^{234}Th); and 2) preferential leaching of ^{234}U from alpha-recoil tracks which are embedded as a result of direct ejection of ^{234}U from adjacent grains.

Figure 2. The hypothetical progression of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residue during the removal of non-detrital matter from the detrital minerals (modified from Lee, 2009).

Figure 3A) ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the solid residues; B) The percentage of U extracted in reagent solutions (relative to the amount of U in the untreated sample). All error bars represent 2σ internal standard error. Operationally-defined fractions are defined: exchangeable (F1), acid-soluble (F2), reducible (F3), oxidisable (F4) and refractory (F5). Error shown represents 2σ internal standard error.

Figure 4A) ($^{234}\text{U}/^{238}\text{U}$) activity ratios of the solid residues following mild HF/ HCl etching in Exp. 3 on the soil sample (diamonds), river sediment (filled circles), marine sediment (unfilled circles) and rock standard BCR-2 (squares); B) The percentage of U extracted in reagent solutions in Exp. 3 using the soil sample (relative to the amount of U in the untreated sample). All error bars represent 2σ internal standard error and most are hidden by markers.

Figure 5. Relative volume change as a function of particle size following: sequential extraction in Exp. 1, compared to the $<63\text{ }\mu\text{m}$ fraction of the untreated soil, and mild HF/ HCl etching in Exp. 3 (24 h), compared to the particle-size distribution following sequential extraction in Exp. 1.