

University of Wollongong

Research Online

Faculty of Science, Medicine and Health -
Papers: part A

Faculty of Science, Medicine and Health

1-1-2014

Assessment of a sequential phase extraction procedure for uranium-series isotope analysis of soils and sediments

P O. Suresh

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

A Dosseto

University of Wollongong, tonyd@uow.edu.au

H K. Handley

Macquarie University

P P. Hesse

Macquarie University

Follow this and additional works at: <https://ro.uow.edu.au/smhpapers>



Part of the [Medicine and Health Sciences Commons](#), and the [Social and Behavioral Sciences Commons](#)

Recommended Citation

Suresh, P O.; Dosseto, A; Handley, H K.; and Hesse, P P., "Assessment of a sequential phase extraction procedure for uranium-series isotope analysis of soils and sediments" (2014). *Faculty of Science, Medicine and Health - Papers: part A*. 1293.
<https://ro.uow.edu.au/smhpapers/1293>

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

Assessment of a sequential phase extraction procedure for uranium-series isotope analysis of soils and sediments

Abstract

The study of uranium-series (U-series) isotopes in soil and sediment materials has been proposed to quantify rates and timescales of soil production and sediment transport. Previous works have studied bulk soil or sediment material, which is a complex assemblage of primary and secondary minerals and organic compounds. However, the approach relies on the fractionation between U-series isotopes in primary minerals since they were liberated from the parent rock via weathering. In addition, secondary minerals and organic compounds have their own isotopic compositions such that the composition of the bulk material may not reflect that of primary minerals. Hence, there is a need for a sample preparation procedure that allows the isolation of primary minerals in soil or fluvial sediment samples. In this study, a sequential extraction procedure to separate primary minerals from soils and sediments was assessed. The procedure was applied to standard rock sample powders (TML-3 and BCR-2) to test whether it introduced any artefactual radioactive disequilibrium. A new step was introduced to remove the clay-sized fraction ($<2\mu\text{m}$). Significant amounts (5–14%) of U and Th were removed from the rock standards during the procedure. No significant alteration in $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios of the rock standards occurred during the procedure. Aliquots of soil sample were subjected to the sequential extraction process to test how each step modifies the uranium-series activity ratios and mineralogy. Although no secondary minerals were detected in the unleached soil aliquots, the sequential leaching process removed up to 17% of U and Th and modified their activity ratios by up to 3%. The modification of the activity ratios poses a demand for careful means to avoid redistribution of isotopes back to the residual phase during phase extraction.

Keywords

assessment, procedure, sequential, uranium, series, isotope, analysis, soils, sediments, phase, extraction

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

Publication Details

Suresh, P. O., Dosseto, A., Handley, H. K. & Hesse, P. P. (2014). Assessment of a sequential phase extraction procedure for uranium-series isotope analysis of soils and sediments. *Applied Radiation and Isotopes*, 83 (Part A), 47-55.

1 1 **Assessment of a sequential phase extraction procedure for uranium-series isotope**
2 2 **analysis of soils and sediments**
3
4 3
5
6
7 4 P. O. Suresh^{1*‡}, A. Dosseto², H. K. Handley³ and P. P. Hesse¹
8
9
10 5 ¹Department of Environment and Geography, Macquarie University, Sydney, Australia
11
12 6 ²GeoQuEST Research Centre, School of Earth and Environmental Sciences, University of Wollongong,
13 7 Australia
14
15
16 8 ³GEMOC, Department of Earth and Planetary Sciences, Macquarie University, Sydney, Australia
17
18 9
19
20
21 10 * Corresponding author: suresh.puthiyaveetil-othayoth@mq.edu.au
22
23 11
24
25 12 ‡Current Address
26
27 13 Institute of Earth Sciences, Academia Sinica, Nangang, Taipei - 11529 Taiwan
28
29
30 14
31
32
33 15
34
35
36 16
37
38 17
39
40
41 18
42
43
44 19
45
46 20
47
48
49 21
50
51
52 22
53
54 23
55
56
57 24
58
59
60 25
61
62
63
64
65

Abstract

The study of uranium-series (U-series) isotopes in soil and sediment materials has been proposed to quantify rates and timescales of soil production and sediment transport. Previous works have studied bulk soil or sediment material, which is a complex assemblage of primary and secondary minerals and organic compounds. However, the approach relies on the fractionation between U-series isotopes in primary minerals since they were liberated from the parent rock via weathering. In addition, secondary minerals and organic compounds have their own isotopic compositions such that the composition of the bulk material may not reflect that of primary minerals. Hence, there is a need for a sample preparation procedure that allows the isolation of primary minerals in soil or fluvial sediment samples. In this study, a sequential extraction procedure to separate primary minerals from soils and sediments was assessed. The procedure was applied to standard rock sample powders (TML-3 and BCR-2) to test whether it introduced any artefactual radioactive disequilibrium. A new step was introduced to remove the clay-sized fraction ($< 2 \mu\text{m}$). Significant amounts (5 to 14%) of U and Th were removed from the rock standards during the procedure. No significant alteration in $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios of the rock standards occurred during the procedure. Aliquots of a soil sample were subjected to the sequential extraction process to test how each step modifies the uranium-series activity ratios and mineralogy. Although no secondary minerals were detected in the unleached soil aliquots, the sequential leaching process removed up to 17% of U and Th and modified their activity ratios by up to 3%. The modification of the activity ratios poses a demand for careful means to avoid redistribution of isotopes back to the residual phase during phase extraction.

Keywords

Sequential extraction, U-series, sediments, clay separation

1. Introduction

Chemical weathering plays a major role in the evolution of the Earth's surface. As such, it is important to constrain timescales of weathering processes during soil production and sediment transfer to better understand rates of landscape evolution. Over the past decade, uranium-series (U-series) isotopes have been used to determine the production rates of soil from bedrock and the transport rates of sediments (e.g., Suresh et al., 2013; Vigier and Bourdon, 2011; Granet et al., 2010; Chabaux et al., 2008; Dosseto et al., 2012, 2008, 2006; DePaolo et al., 2006; Dequincey et al., 2002; Vigier et al., 2001; Rosholt, 1982). U-series isotopes are ideal tools to constrain such timescales as they fractionate during rock-water interaction and their decay rate is such that radioactive disequilibrium operates on timescales similar to that of weathering processes. For a system closed for more than one million years (e.g. bedrock older than lower-Pleistocene), the ^{238}U - ^{234}U - ^{230}Th isotope system will be in secular equilibrium; i.e., the parent-daughter activity ratios will be 1. During weathering, ^{234}U may be preferentially leached from damaged crystal lattice sites created by the high energy alpha decay of ^{238}U (Rosholt, 1982). Additionally, if the decay of ^{238}U occurs near the surface of a soil or sediment grain, a fraction of the intermediate nuclide, ^{234}Th (parent of ^{234}U), may be ejected out of the grain due to the recoil energy of the decay, decreasing the ($^{234}\text{U}/^{238}\text{U}$) (herein, a ratio in parentheses denotes the activity ratio) (Kigoshi, 1971). In oxidising conditions, U will have an oxidation state of +6 and form the uranyl ion, $\text{U}_{\text{VI}}\text{O}_2^{2+}$, which is stabilized by highly soluble carbonate complexes at pH 5 to 8 (Langmuir, 1978). Th will be present as Th^{4+} , which is water-insoluble (at pH near 7). The difference in solubility, and hence mobility, causes elemental fractionation between U and Th, which contributes to the radioactive disequilibrium between ^{230}Th and ^{234}U . Since the activities of the isotopes are time dependent, it is possible to model their evolution in weathering profiles and sediments over time (Suresh et al., 2013; Dosseto et al., 2012, 2011, 2008, 2006; Chabaux et al., 2003; Dequincey et al., 2002; Vigier et al., 2001). Two approaches are used to estimate weathering timescales using U-series isotopes. The first utilises the fractionation of U and Th isotopes due to their differences in chemical mobility. The second approach uses the isotopic fractionation of ^{238}U and ^{234}U created by the recoil loss of ^{234}U from the surface of grains.

The recoil length for the high energy alpha decay of ^{238}U is ~30 nm in most silicate minerals (Hashimoto et al., 1985; Kigoshi, 1971; Turkowsky, 1969) and therefore this fractionation is only measurable in grains of a few tens of micrometers or less. The measured ^{234}U - ^{238}U disequilibrium can be used to estimate the formation age (comminution age) of the grains following the comminution approach of DePaolo et al. (2006). This approach has been used to determine rates of soil formation and timescales of sediment transport and their relationships to past climate changes (Dosseto et al., 2010; Lee et al., 2010; Suresh et al., 2010; DePaolo et al., 2006).

The approaches discussed above are based theoretically on the evolution of U-series isotopes in primary mineral grains since the onset of bedrock weathering, assuming that these isotopes are in secular equilibrium prior to weathering, i.e., that the bedrock is older than 1 Ma. However, several previous studies (e.g., Suresh et al., 2013; Dosseto et al., 2012, 2008, 2006; Dequincey et al., 2002) have analysed bulk soils and/or sediments, which are complex mixtures of primary minerals, secondary phases and organic materials. Separation of primary minerals from the bulk material for U-series analysis is expected to significantly improve the accuracy of the results obtained from the approaches described above. Efforts have been made to separate primary minerals for the comminution age approach using U isotopes by Dosseto et al. (2010), Lee et al. (2010) and Suresh et al. (2010). However, the effect of the leaching procedure and separation of clay-sized fraction on the U-series isotopes of the primary minerals still needs to be tested.

In order to test the reliability and examine the effects on nuclide activity ratios and elemental concentrations of phase extraction procedures proposed here to isolate the primary mineral grains of soil/sediments, we have carried out sequential leaching of soil sample aliquots using a procedure adopted and slightly modified from Schultz et al. (1998) to remove exchangeable and adsorbed fractions, organic materials, carbonates, and amorphous and crystalline Fe-Mn oxides (Table 1). We have added an additional step to physically remove the clay-sized particles by centrifugation (discussed in detail below). The residues from each step of the sequence were analysed for mineralogy, U and Th elemental and isotopic composition and particle size distribution to assess the effects of the removal of the different phases. In addition, powdered standard rock samples were subjected to the same sequential leaching and clay-size fraction removal procedure to assess whether the procedure induces any isotopic fractionation.

2. Materials and Method

In order to determine whether the sequential leaching and clay separation procedure itself produces radioactive disequilibrium, we analysed USGS geochemical reference materials TML-3 and BCR-2. TML-3 (Table Mountain Latite) is a Pliocene lava from Sonora, California, which has U-series isotopes in secular equilibrium (Sims et al., 2008; Turner et al., 2001; Williams et al., 1992). BCR-2 (Basalt Columbia River) also has U-series isotopes in secular equilibrium (Prytulak et al., 2008; Hoffman et al., 2007). Both standards were subjected to the sequential leaching and clay removal procedure. A soil sample from a previously studied weathering profile, developed over granitic bedrock at Frogs Hollow, south-eastern Australia (Suresh et al., 2013, 2010) was used to investigate how the mineralogical, elemental and isotopic composition of soil material evolves during sequential leaching and the selective removal of different phases. The Frogs Hollow soil sample is ideal for such a study as secondary phases were not detectable by X-ray diffraction (XRD), which therefore, permits determination of how the leaching and clay-separation procedure affects U-series isotopes in primary minerals in soil.

All reagent solutions were prepared using Millipore Milli-Q water with 18.2 MΩ.cm resistivity. Acid-washed polypropylene bottles were used for the storage of solutions. To remove exchangeable, adsorbed and organic phases from the soil, a solution of sodium hypochlorite in hydrochloric acid was prepared, using Merck Ultrapur sodium hypochlorite (6-14% strength) and Teflon distilled hydrochloric acid (Table 1). Sodium acetate solution, prepared with Merck Suprapur® sodium acetate and 99.7% pure acetic acid supplied by BDH Chemicals, was used to remove the carbonate fraction from soil. Amorphous and crystalline oxides of Fe and Mn were removed using a solution of hydroxylamine hydrochloride, prepared from ≥ 99% pure hydroxylamine hydrochloride supplied by Fluka. LR grade sodium hexametaphosphate manufactured by Chem-Supply was used to prepare a dispersant for separation of the clay fraction from soil.

The soil sample was first dry-sieved at 500 μm and then wet-sieved at 53 μm with de-ionized water without pre-soaking, agitation or dispersion. The <53 μm sieved fraction was dried and then homogenised using an agate pestle and mortar. Approximately 2 g of soil material was placed in a pre-cleaned 50 ml polypropylene centrifuge tube. After each leaching step given below, the mixture was centrifuged at 7000 rpm for 15 minutes and the

supernatant was discarded using a pipette. The material was then rinsed twice with 10 ml of 18.2 MΩ.cm Milli-Q water, followed by centrifugation at 7000 rpm for 15 minutes and then careful removal of the supernatant using a pipette. To obtain leached material representative of each step of the leaching procedure sequential leaching was performed on four aliquots (FL1-FL4) for which the leaching stages carried out for each sample are detailed in Table 2. Another aliquot of starting material, FLC, (Table 2) was not chemically leached but had the clay-sized fraction removed by centrifugation. The final aliquot did not undergo any stage of the sequential extraction procedure prior to U-series analysis.

The order of extraction of the phases within the procedure is important for the effectiveness of the method (Miller et al., 1986; Shultz et al., 1998). The order of phase extraction used in this study is based on Shultz et al. (1998) and is given in Table 1. Schultz et al. (1998) suggest extraction of the organic fraction immediately after the extraction of the exchangeable fraction, as the thin organic coating on the grains can inhibit the action of reagents used to remove other phases, if performed before organic removal. Schultz et al. (1998) reported that ~ 50% of exchangeable uranium is re-adsorbed when MgCl₂ is used for extraction of exchangeable phases, and therefore that reagent was not used here. We performed removal of exchangeable, adsorbed and organic phases together, using a solution of NaOCl at pH 7.5. An electrolyte prepared from a salt of a strong acid and base or a weak acid and base at pH ~7 can be used for removal of exchangeable fraction from soil (Rauret, 1998). The weak complexing ability of Cl⁻ ions in the solution will be sufficient to dissolve the heavy metals weakly bound to the surface of the soil grains (Gleyzes et al., 2002). The use of NaOCl causes re-adsorption of uranium during leaching, but the oxidising nature of NaOCl in the solution is expected to convert the reduced form of uranium to the more soluble oxidised form (Duff et al., 1998). The removal of the adsorbed, exchangeable and organic fractions was accomplished using a solution of 6-14% sodium hypochlorite (15 ml per gram of sample) adjusted to pH 7.5 with 9 M HCl (Table 1). The mixture of the sample and the reagent was heated at 90 °C for 30 minutes. This step was repeated to ensure complete removal of organic matter. The carbonate fraction was removed by treating the sample with a 1 M solution of sodium acetate, adjusted to pH 4 with acetic acid (Table 1). The mass ratio of reagent to reactant was 10:1. The mixture was agitated for two hours on a Ratek roller mixer at 30 rpm. This step was repeated twice to ensure complete removal of carbonates. Amorphous and crystalline Fe and Mn oxides were then removed from the sample with a solution of 0.04 M hydroxylamine hydrochloride (Table 1). The mass ratio of reagent to

184 reactant was 10:1. The mixture was thoroughly mixed for 5 hours using a Ratek roller mixer
185 at a speed of 30 rpm.

186 Secondary clay minerals will have the U-series isotopic signature of the pore water
187 they precipitate from, which is typically characterised by high ($^{234}\text{U}/^{238}\text{U}$) (Plater et al.,
188 1992). Therefore, it is necessary to remove such material from the sample in order to obtain
189 only the primary mineral grains of interest. Many secondary minerals are very fine grained
190 and may include oxides (e.g. of iron), carbonates, silicates (such as clay minerals) and other
191 phases. Consequently, we have added an additional step to the phase extraction procedure of
192 Schultz et al. (1998) to remove the clay fraction of the sample. Note that here the term clay
193 refers to its granulometrical definition, and not mineralogical definition, i.e., particles $< 2\ \mu\text{m}$
194 in size, but that this size-fraction will contain the fine-grained secondary (mineralogical) clay
195 material. The method used to remove the clay-sized fraction was adopted from the
196 centrifugation method detailed in the USGS laboratory manual for X-Ray powder diffraction
197 (Poppe et al., 2001). Using this procedure, all particles of $< 2\ \mu\text{m}$ diameter, including any
198 primary minerals, are removed. A solution of 5% sodium hexametaphosphate was added to
199 the sample material to disperse the particles. The mixture was subsequently sonicated with an
200 ultrasonic probe for 20 seconds at a power of 190 W. It was then thoroughly agitated
201 overnight on a Ratek roller mixer at 30 rpm. The size fraction of $< 2\ \mu\text{m}$ was then removed
202 through controlled centrifugation by centrifuging the mixture at 1500 rpm for 34 s and
203 stopped using a brake time of 13 s. The duration of centrifugation and stopping of the
204 Heraeus Biofuge Primo centrifuge were calculated using USGS guidelines (Poppe et al.,
205 2001). The supernatant was then carefully removed by pipette. The samples were
206 subsequently centrifuged with Milli-Q water at the same speed and for the same duration, the
207 supernatant was removed by pipette. This latter Milli-Q water stage was repeated until the
208 supernatant was clear (usually 3–4 times). Samples were then dried in a dust-free oven,
209 homogenized in an agate mortar and then sub-sampled for XRD and uranium-series analysis.
210 The sequential leaching and clay separation procedure is summarized in Table 1.

211 Particle size distributions of the samples were obtained using a Malvern Mastersizer
212 instrument with de-ionized water as the dispersant medium. The mineralogy of the samples
213 were determined by X-ray diffraction using a PANalytical X'pert PRO MPD diffractometer
214 with a 45 kV, 40 mA $\text{CuK}\alpha$ radiation X'celerator detector and Bragg Brentano geometry.
215 Scans were conducted from 5 to $50^\circ 2\theta$, at $5^\circ 2\theta/\text{min}$. Highscore Plus software version 2.2.4
216 with the ICDD PDF2 database by PANalytical was used for mineral identification. The basic

Rietveld refinement option available in the software was used to quantify the minerals detected.

Approximately 100 mg of each sample for uranium-series analysis was spiked with ~ 30 mg of ^{236}U - ^{229}Th tracer solution and then digested using a mixture of HCl, HNO₃, HF and HClO₄. The samples were left at room temperature for 30 minutes for reaction in closed Teflon beakers and then heated at 130 °C overnight. Sample – tracer equilibration starts immediately during the reaction and will continue throughout the procedure. The mixture was dried at 100 °C for ~ 5 hours and then dried down at 200 °C. The samples were then taken up in 7 M HNO₃ in acid-washed 15 ml centrifuge tubes and centrifuged at 4000 rpm for 15 minutes to check that the sample had digested fully. If not, the residue was redigested and added to the solution. This solution was then loaded on chromatographic columns containing AG1X8 anionic resin for the separation of U and Th (Sims et al. 2008; Dosseto et al. 2006). U and Th isotopic analyses were performed using a Nu instrument MC-ICPMS, following the method detailed in (Sims et al. 2008). The U analyses were bracketed with CRM U010 isotopic standard. CRM U005-A standard was analysed as an unknown to carry out linear drift correction and to check the normalization of the U isotope measurements of the sample. For Th, all samples were bracketed with the OU Th ‘U’ isotopic reference material for linear drift correction (Sims et al., 2008). The UCSC Th ‘A’ standard was analysed as an unknown. The values of standards measured as unknowns were within 3 ‰ of the recommended values (Sims et al., 2008). The procedural blank for Th was 70 pg and for U it was 20 pg. An unleached TML-3 rock standard was analysed to measure accuracy, which was 1.1% for Th concentration, 0.06% for U concentration, 0.6% for ($^{234}\text{U}/^{238}\text{U}$) and 0.24% for ($^{230}\text{Th}/^{238}\text{U}$). Reproducibility was measured by replicate analysis of unleached TML-3, which was 0.9% for Th concentration, 1.8% for U concentration, 0.17% for ($^{234}\text{U}/^{238}\text{U}$) and 1% for ($^{230}\text{Th}/^{238}\text{U}$).

3. Results

3.1. Rock standards

Uranium and thorium elemental and isotopic data are presented in Table 3 and Figs. 1 and 2. The TML-3 aliquots T1 and T2, which did not undergo sequential leaching or clay-sized fraction separation (here after referred to as ‘unleached’), have ~ 15 % higher U and Th

concentration than TL1 and TL2 which were sequentially leached and had the $< 2 \mu\text{m}$ size fraction removed (here after referred to as ‘leached’) (Fig. 1). The weighted average values for Th and U concentrations in TML-3 from an inter-laboratory study (Sims et al., 2008) are within the range of the values measured here for the unleached samples. The Th concentrations of unleached BCR-2 samples B1 and B2 are $\sim 20 \%$ higher than those in the leached aliquots BL1 and BL2. B1 and B2 have U concentrations 1.612 ± 0.001 and 1.637 ± 0.001 ppm whereas the leached aliquots contain 1.50 ± 0.001 and 2.99 ± 0.005 ppm U respectively. The weighted average values for Th and U concentrations in BCR-2 from an inter-laboratory study (Sims et al., 2008) are 5.86 ± 0.08 ppm and 1.69 ± 0.03 ppm, respectively.

The unleached (T1, T2) and one of the leached (TL1) TML-3 aliquots yield ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) close to secular equilibrium and within $\sim 8 \%$ deviation from the interlaboratory average TML-3 ratios reported by Sims et al. (2008). The other leached aliquot TL2 yields a ($^{234}\text{U}/^{238}\text{U}$) ratio deviating by 21% from secular equilibrium ratio (Fig. 2a). Both the BCR-2 unleached (B1, B2) and leached aliquots (BL1, BL2) have ($^{234}\text{U}/^{238}\text{U}$) close to secular equilibrium (1.003 for the unleached aliquot; 1.007 - 1.008 for the leached aliquots). The ($^{230}\text{Th}/^{238}\text{U}$) of the leached aliquot BL2 is significantly different from the expected value of 1 . This aliquot contains ~ 2 times higher concentration of U compared to the other aliquots.

3.2. Soil samples

The unleached soil aliquot (FLU) has a particle size distribution with a modal diameter of $30.7 \mu\text{m}$ and a clay-sized fraction ($< 2 \mu\text{m}$) of $10.8 \text{ wt. } \%$ (Table 2). The modal diameter of the aliquot that has undergone the entire procedure, including removal of the clay-sized fraction (FL4), is $32.7 \mu\text{m}$ but still with $5.2 \text{ wt. } \%$ clay-sized material. The aliquot where only the clay removal was undertaken (FLC) has a modal particle diameter of $30.5 \mu\text{m}$ and a clay-sized fraction of $4.9 \text{ vol. } \%$. SEM (Scanning Electron Microscopy) images of the unleached aliquot (FLU) and the fully-processed aliquot (FL4) are shown in Fig. 3.

The unleached soil aliquot consists of $69.3 \text{ wt. } \%$ quartz, $16.9 \text{ wt. } \%$ albite and $13.7 \text{ wt. } \%$ microcline (Table 2). At every step of the leaching procedure, the abundance of minerals varies by less than 2% compared to the initial mineral abundance (Fig. 4). Authigenic phases were not detected by XRD in any of the leached or unleached aliquots.

U and Th elemental and isotopic data are shown in Table 2 and Figs. 5 and 6. Overall, there is an 11 % decrease in Th content through the leaching procedure. However both the sodium hypochlorite wash step and the hydroxylamine hydrochloride leaching step, the Th content of the residue increased. The Th content of FLC, subjected only to clay removal was somewhat higher than the fully leached sample FL4. A similar pattern also holds with respect U content, however, the largest decrease in U concentration occurs in the final clay removal step (FL4) and the resulting U concentration is similar to that of the sample subject to clay fraction removal alone (FLC) (Fig. 5).

The activity ratios decreased over the leaching procedure although increases were also measured at some steps. ($^{234}\text{U}/^{238}\text{U}$) decreased most significantly at the clay fraction removal step while ($^{230}\text{Th}/^{238}\text{U}$) decreased most dramatically with the removal of exchangeable, adsorbed and organic matter. In both the cases the final activity ratios (FL4) are similar to the values of FLC, subjected only to clay fraction removal (Fig. 6).

4. Discussion

The measurements of U and Th concentrations of the unleached rock standards are within the 2σ acceptable limits of their published values. The Th concentrations of the unleached TML-3 aliquots T1 and T2 are within ± 4.43 ‰ and U concentrations are within -9.1 and 9.1 ‰ from those reported by Sims et al. (2008). For the unleached BCR – 2 aliquots, B1 is -1.3 ‰ and B2 is +1.3 ‰ compared with the Th concentration values published by Sims et al. (2008), and within 2.5 ‰ of each other. U concentrations for B1 and B2 are within -7.7 and 7.7 ‰ of that published by Sims et al. (2008) and within 15.5 ‰ of each other (Fig. 1).

The U-series elemental and isotopic data of the rock standards show that the sequential extraction procedure performed resulted in significant loss of U and Th. This amounted to < 14 wt. % loss of U from TML – 3 and 7.4 wt. % loss of U from one of the BCR-2 leached rock standards relative to the mean U concentration in the unleached rock standards. The second leached BCR-2 standard lost 17 wt. % of Th but gained about 84 wt. % U. This unexpected result is discussed in detail below. The general loss of Th and U may be attributed to the dissolution of primary minerals and/or removal of the < 2 μm size fraction. Surface etching of primary minerals by dissolution occurs in the presence of weak organic

acids (Welch and Ullman, 1993; Huang and Keller, 1970) and hence the removal of U and Th is possible during leaching. Also, during the separation of the $< 2\mu\text{m}$ fraction, platy and lower density minerals may be removed preferentially, as these minerals may not settle as expected during centrifuging. This preferential removal may also account for the loss of U and Th, as the content of U and Th in different minerals is expected to be different.

One of the BCR-2 leached aliquots gave a U concentration 77% higher and Th concentration 22% lower than the interlaboratory value (Sims et al. 2008). The aliquot was re-analyzed and yielded similar concentrations (4.48 ppm Th and 2.87 ppm U) which rules out the possibility of analytical problems during analysis by ICPMS. Such a large deviation from accepted U-Th concentration values could possibly result from incomplete sample/tracer equilibration. Similar problems were reported by Pin and Zalduegui (1997) during processing samples for rare earth elements, U and Th. They attributed the problem to incorporation of some of the elements in the tracer to the early stage intermediates of the reaction between the sample and the reagents, which then were not available for equilibration. Formation of stable complex fluorides during dissolution of samples rich in alkaline earth and/or aluminium may mask the U and Th before a full isotopic exchange between sample and tracer occurs (Pin and Zalduegui, 1997). The $^{236}\text{U}/^{238}\text{U}$ atomic ratio measured by the mass spectrometer for the problematic leached BCR – 2 sample (4.79×10^{-5}) is less than half of that measured for the other leached BCR-2 aliquot (1.0879×10^{-4}) and the unleached aliquot (1.01679×10^{-4}), where the amount of sample digested, amount of tracer added and all other measured atomic ratios are similar. The $^{229}\text{Th}/^{232}\text{Th}$ atomic ratio for the leached aliquot of BCR-2 sample with lower concentration of elemental Th is 6.493×10^{-5} , whereas for the other leached aliquot it is 7.607×10^{-5} and for the unleached aliquot it is 7.30×10^{-5} , confirming the possibility of an incomplete sample-tracer equilibration, although all the TML-3 and BCR-2 aliquots were processed in a similar manner following tracer addition to the sample. Palmer and Edmond (1993) also reported problems due to poor sample/tracer equilibration during U-Th analysis of water samples.

A 2σ precision of 8 ‰ in the measured ($^{234}\text{U}/^{238}\text{U}$) activity ratio of rock standards is considered acceptable with the measurement method used at Geochemical Evolution of Metallogeny Of Continents (GEMOC) laboratory (Turner et al., 2011). All the leached and unleached standard aliquots except one of the leached TML-3 have their ($^{234}\text{U}/^{238}\text{U}$) within this limit when compared to the ratios reported by Sims et al. (2008). The ($^{230}\text{Th}/^{238}\text{U}$) - of all the leached and unleached TML – 3 aliquots and the unleached BCR-2 and one of the leached

aliquots (BL2) are within a 2σ deviation of $\sim 33\%$ of the value published by Sims et al. (2008). The accepted 2σ precision for ($^{230}\text{Th}/^{238}\text{U}$) measurements in rock standards at GEMOC is 2 % (Turner et al., 2011). The very low value of ($^{230}\text{Th}/^{238}\text{U}$) of BL1 is due to the anomalously high concentration of U measured in it, most likely due to the poor sample-tracer equilibration, as discussed above. When compared to the results of U-series activity ratios of TML – 3 and BCR – 2 standards published by Sims et al. (2008), and considering the accepted 2σ precisions by Turner et al. (2011), it can be observed that the leaching and fine-fraction removal procedure employed to the rock standards does not impart any artefactual U-series disequilibrium.

The median particle size of the soil sample does not seem to be affected by the clay-size fraction separation step. However, the aliquot subjected to sequential leaching and removal of the clay-sized fraction (FL4) showed a small increase (6%, compared to 3% reproducibility for this instrument) in the median particle size. The minor change median particle size is due to the removal of finer fraction.

The leaching and separation procedure did not affect the relative proportions of the primary minerals in the soil sample. XRD analysis did not detect any secondary phases in the soil sample (detection limit $\sim 1\%$). The mass percentage of primary minerals in the aliquots of all steps of the sequential leaching procedure did not show any significant variation (Fig. 4). The implication is that the leaching procedure used here does not cause alteration to the relative distribution of primary minerals.

The procedure for the removal of the clay-sized fraction will remove particles $< 2\ \mu\text{m}$, regardless of mineralogy. Therefore, even primary minerals within the 0-2 μm size fraction will be removed. As the relative distribution of primary minerals in the residue is not affected by removal of the $< 2\ \mu\text{m}$ fraction, the primary minerals removed have the same relative mineralogical distribution as in the bulk sample. After the clay removal step, half of the $< 2\ \mu\text{m}$ size fraction ($\sim 5\%$ total sample mass) remained in the two aliquots. Townsend (1997) observed breaking down of soil grains during ultrasonic probing, which affected the particle size distribution. Ultrasonication of the sample during the clay-sized fraction removal step may have created smaller grains in excess.

Removal of the exchangeable phases and organic materials resulted in a 7.4 % decrease in U concentration, implying that a significant proportion of U is contained in this phase. No significant change in U concentration was observed after the sodium acetate/acetic

acid leaching step, consistent with the restricted carbonate content (lower than XRD detection limits) of the soil. The U concentration increased by 6.6% after removal of Fe and Mn oxides, showing that there is little or no U in the removed phase. A similar observation was reported by Lee et al. (2004), while leaching soil samples with ammonium acetate. When the leaching procedure was complete 0.9% of U was removed from the sample.

When the clay-size fraction was subsequently removed from the leached sample, U concentration decreased by 17% compared with the previous stage, indicating the presence of a large proportion of U in the size fraction below 2 μm . Complete removal of the clay-size fraction would therefore result in an even greater loss of U. When sequential leaching was complete and clay size fraction was removed, 21 % U had been removed, when compared to the starting material. When only the clay-sized fraction was removed from the soil aliquot without leaching, 22% of U was lost. This shows that a large fraction of U is held in the clay-sized fraction of soil. Lee et al. (2004) and Baeza et al. (1995) also observed increases in the concentration of U-series isotopes with decreasing soil grain size. Baeza et al. (1995), using an empirical relation connecting surface and volume activities of actinides and their ionic size, argued that radionuclides with greatest ionic radii are precluded from incorporating to crystal lattices and hence their concentrations in refractory minerals will be proportional to specific surface area.

The 7.3% increase in Th after removal of the exchangeable and organic fractions may be due to little or no presence of Th in these fractions. Blanco et al. (2004) also reported that Th was present in less than one percent of the organic and exchangeable fractions extracted from soil following the method used by Schultz et al. (1998). During the sodium acetate–acetic acid buffer leaching stage 20.2% of the initial Th was removed, indicating the presence of a large proportion of Th in this leached fraction. Plater et al. (1992) reported removal of up to 8.2 % of Th from river sediments during extraction of carbonate. Testa et al. (1999) also reported extraction of ~ 14 % Th when the carbonate fraction was separated from canal sediments. Our results show that this leaching step can also leach significant amounts of Th even when carbonate minerals are absent or in very low abundance (below XRD detection). The sample used here is from an acidic soil profile of pH = 5.5 (Suresh et al., 2013). It is known that the presence of organic acids increase the mobility of Th from soil (Chabaux et al., 2003). It is possible that the mobilized Th might be readsorbed onto the soil grains of this sample, and remobilized during leaching with the sodium acetate – acetic acid buffer. There was a 9.5% increase in Th concentration of the residue following the removal of Fe and Mn

oxides, indicating little or no presence of Th in the removed fraction. Blanco et al. (2004) also reported that Th was less than one per cent in the Fe and Mn oxide fractions of soil. When removing the clay-size fraction, the Th concentration decreased by 5.1%, indicating the presence of a significant amount of Th in that fraction.

Similarly to U concentration variations, ($^{234}\text{U}/^{238}\text{U}$) vary little over the different steps of the sequential leaching, with a slight increase in ^{234}U depletion throughout the procedure, but show a significant decrease when the $< 2 \mu\text{m}$ fraction is removed. This suggests that the $< 2\mu\text{m}$ fraction has a high ($^{234}\text{U}/^{238}\text{U}$). The ($^{230}\text{Th}/^{238}\text{U}$) shows the same systematic changes, but with a more pronounced increase of the disequilibrium throughout the procedure. The removal of the $< 2\mu\text{m}$ fraction does not seem to significantly decrease further the ($^{230}\text{Th}/^{238}\text{U}$) (compared to FL3 and FLC).

The organic and exchangeable fraction of soil may have ($^{234}\text{U}/^{238}\text{U}$) > 1 (Plater et al., 1992, Chabaux et al., 2003, Dosseto et al., 2008). Removal of the organic/exchangeable materials with ($^{234}\text{U}/^{238}\text{U}$) > 1 from soil then should cause a decrease in the ($^{234}\text{U}/^{238}\text{U}$) of the residue, and the same is observed here. No significant change in the ($^{234}\text{U}/^{238}\text{U}$) was observed after leaching with sodium acetate/acetic acid buffer, again consistent with insignificant or minor presence of carbonate in the sample. Oxides of Fe and Mn in soil will also be characterised by the ($^{234}\text{U}/^{238}\text{U}$) of the soil pore water they precipitate from, which is expected to be > 1 (Dosseto et al., 2008; Plater et al., 1992). Removal of the Fe and Mn oxide fraction from the soil will therefore, decrease the ($^{234}\text{U}/^{238}\text{U}$) of the residue, which was observed here.

The lowest ($^{234}\text{U}/^{238}\text{U}$) in the residue was measured for aliquots that underwent the removal of the clay-sized fraction (FL4 and FLC, Table 2) indicating a higher ($^{234}\text{U}/^{238}\text{U}$) in the removed fraction. Authigenic clays will have the U-isotopic signature of the pore water. Clay minerals formed from the pore water are expected to have ($^{234}\text{U}/^{238}\text{U}$) > 1 , as U will be co-precipitated with clay minerals and/or incorporated into the lattices of clay minerals (Scott, 1968; Mitchell, 1964). However, the soil samples processed here do not have detectable clay minerals; therefore, the clay-sized fraction removed must contain largely primary mineral grains. This fraction has the highest specific surface area in the soil, and may contain the most redistributed uranium from the fluid phase, which is expected to be enriched in ^{234}U due to recoil ejection and preferential leaching (Fleischer, 1982; Kigoshi, 1971). Removal of a fraction with high ($^{234}\text{U}/^{238}\text{U}$) will leave the residue with a lower ($^{234}\text{U}/^{238}\text{U}$), as

is observed here. The residual primary minerals after leaching and clay-fraction removal have a ($^{234}\text{U}/^{238}\text{U}$) of 0.945 ± 0.002 , which is comparable to the ($^{234}\text{U}/^{238}\text{U}$) reported by Plater et al. (1992) for the residual minerals obtained after leaching river bottom sediments.

The ($^{230}\text{Th}/^{238}\text{U}$) increased significantly when the exchangeable and organic fractions were removed. This suggests that the removed fraction has a very low ($^{230}\text{Th}/^{238}\text{U}$). During sequential leaching of river sediments, Plater et al. (1992) also reported ($^{230}\text{Th}/^{238}\text{U}$) as low as 0.723 ± 0.362 in extracted organic matter. When the sodium acetate/acetic acid leaching step was performed, the ($^{230}\text{Th}/^{238}\text{U}$) decreased in the residue, indicating a ratio of > 1 in the removed fraction, which is consistent with the observations reported by Plater et al. (1992), when sediment samples were leached to extract carbonate fraction. They also reported that Fe and Mn oxides in the sediments contained ($^{230}\text{Th}/^{238}\text{U}$) > 2 . Removal of a fraction with a higher ($^{230}\text{Th}/^{238}\text{U}$) than the equilibrium value will leave the residue with a ($^{230}\text{Th}/^{238}\text{U}$) of < 1 , and the same was observed here. Removing the clay-sized fraction from the residue again increased the ($^{230}\text{Th}/^{238}\text{U}$), indicating that the ratio in the removed fraction is lower than the residue from the previous step.

In summary, when the sequential extraction procedure for removal of different phases is applied to a soil sample with little or no secondary phases, the U-series isotope ratios vary in a similar way to that observed with soil/sediment samples containing secondary phases (Blanco et al., 2004; Lee et al., 2004; Schultz et al., 1998; Plater et al., 1992).

5. Conclusions

The modified sequential extraction procedure for primary minerals in soils was tested with rock standard samples and a natural soil sample. A considerable amount of U and Th is removed from the standard rock samples during the procedure. The measured U-series activity ratios were within the accepted precision levels from the values published, with one exception due to possible problems during sample preparation. This indicates that the procedure does not induce artefactual disequilibrium to the sample. The mass percentage of the primary minerals in the soil sample did not vary significantly during the stages of phase extraction, which indicates that the procedure does not affect the relative distribution of primary minerals in the sample. Even though secondary phases or clay minerals were not detected in the soil sample by XRD, the removal of U-series isotopes during the sequential extraction procedure tends to modify the ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) from their unleached sample values. The possibilities of re-adsorption of U back to the residual phases during

leaching needs more investigation. Unaccounted removal of U and/or Th from soil and sediment samples during sequential leaching could lead to erroneous estimation of sediment dynamic timescales using U-series models.

Acknowledgements:

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

We thank the two reviewers for their constructive reviews and A. Harms for editorial handling of the manuscript.

POS acknowledges an iMQRES scholarship supporting this research.

AD acknowledges an ARC future fellowship FT0990447.

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

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

References

- Baeza, A., Del Rio, M., Jimenez, A., Miro, C., and Paniagua, J., 1995, Influence of geology and soil particle size on the surface-area/volume activity ratio for natural radionuclides. *Journal of Radioanalytical and Nuclear Chemistry*, 189, 289-299.
- Blanco, P., Tomé, F.V., and Lozano, J.C., 2004, Sequential extraction for radionuclide fractionation in soil samples: a comparative study. *Applied Radiation and Isotopes*, 61, 345-350.
- Chabaux, F., Riotte, J. and Dequincey, O., 2003, U-Th-Ra fractionation during weathering and river transport, In: B. Bourdon, G.M. Henderson, C.C. Lundstrom, S.P. Turner, (Eds), *Uranium-series Geochemistry, Reviews in Mineralogy and Geochemistry* 52, Geochemical Society - Mineralogical Society of America, pp. 533-576.
- Chabaux, F., Bourdon, B., and Riotte, J., 2008, U-Series Geochemistry in Weathering Profiles, *River Waters and Lakes. Radioactivity in the Environment*, 13, 49-104.
- DePaolo, D.J., Maher, K., Christensen, J.N., and McManus, J., 2006, Sediment transport time measured with U-series isotopes: Results from ODP North Atlantic drift site 984. *Earth and Planetary Science Letters*. 248, p. 394-410.
- Dequincey, O., Chabaux, F., Clauer, N., Sigmarsson, O., Liewig, N., and Leprun, J.C., 2002, Chemical mobilizations in laterites: Evidence from trace elements and ^{238}U - ^{234}U - ^{230}Th disequilibria. *Geochimica et Cosmochimica Acta*, 66, 1197-1210.
- Dosseto, A., Buss, H., and Suresh, P.O., 2012, Rapid regolith formation over volcanic bedrock and implications for landscape evolution. *Earth and Planetary Science Letters*, 337-338, 47 – 55.
- Dosseto, A., Buss, H., and Suresh, P.O., 2011, The delicate balance between soil production and erosion, and its role on landscape evolution. *Applied Geochemistry*, 26, Supplement, S24-S27.
- Dosseto, A., Hesse, P.P., Maher, K., Fryirs, K., and Turner, S., 2010, Climatic and vegetation control on sediment dynamics during the last glacial cycle. *Geology*, 38, 395-398.
- Dosseto, A., Turner, S.P., and Chappell, J., 2008, The evolution of weathering profiles through time: New insights from uranium-series isotopes. *Earth and Planetary Science Letters*, 274, 359-371.
- Dosseto, A., Turner, S.P., and Douglas, G.B., 2006, Uranium-series isotopes in colloids and suspended sediments: Timescale for sediment production and transport in the Murray–Darling River system. *Earth and Planetary Science Letters*, 246, 418-431.
- Duff, C. M., Mason, C. F. V., and Hunter, D. B., 1998, Comparison of acid and base leach for the removal of uranium from contaminated soil and catch-box media. *Canadian Journal of Soil Science*, 78, 675-683.
- Fleischer, R.L., 1980. Isotopic disequilibrium of uranium: Alpha-recoil damage and preferential solution effects. *Science*, 207, 979-981.
- Fleischer, R. L., 1982, Alpha-recoil damage and solution effects in minerals: uranium isotopic disequilibrium and radon release. *Geochimica et Cosmochimica Acta*, 46, 2191 -2201.
- Gleyzes, C., Tellier, S., and Astruc, M., 2002, Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *Trends in Analytical Chemistry*, 21, 451-467.
- Granet, M., Chabaux, F., Stille, P., Dosseto, A., France-Lanord, C., Blaes, E., 2010. U-series disequilibria in suspended river sediments and implication for sediment transfer time in alluvial plains: The case of the Himalayan rivers. *Geochim. Cosmochim. Acta* 74, 2851-2865.
- Hashimoto, T., Aoyagi, Y., Kudo, H., and Sotobayashi, T., 1985, Range calculation of alpha-recoil atoms in some minerals using LSS-theory. *Journal of Radioanalytical and Nuclear Chemistry*, 90, 415-438.
- Hoffman, D. L., Prytulak, J., Richards, D. A., Elliot, T., Coath, C. D., Smart, P. L., and Scholz, D., 2007, Procedures for accurate U and Th isotope measurements by high precision MC-ICPMS. *International Journal of Mass Spectrometry*, 264, 97-109.

- Huang, W. H., and Keller, W. D., 1907, Dissolution of rock-forming silicate minerals in organic acids: simulated first-stage weathering of fresh mineral surfaces. *The American Mineralogist*, 55, 2076-2094.
- Kigoshi, K., 1971, Alpha-Recoil Thorium-234: Dissolution into Water and the Uranium-234/Uranium-238 Disequilibrium in Nature. *Science*, 173, 47-48.
- Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochimica et Cosmochimica Acta* 42, 547-569.
- Lee, M.H., Yoon, Y.Y., Clark, S.B., and Glover, S.E., 2004, Distribution and geochemical association of actinides in a contaminated soil as a function of grain size, *Radiochimica Acta*, , 92, , 671-675.
- Lee, V. E., Chapter 3, Radiogenic isotope geochemistry and the evolution of earth's surface and interior. 2009, PhD Thesis, University of California, Berkeley.
- Lee, V.E., DePaolo, D.J., and Christensen, J.N., 2010, Uranium-series comminution ages of continental sediments: Case study of a Pleistocene alluvial fan. *Earth and Planetary Science Letters*, 296, 244-254.
- Mitchell, R. L., 1964, Trace elements in soils, In: F. E. Bear (Ed.) *Chemistry of the soil*, Reinhold publishing corporation, New York.
- Miller, W. P., Martens D. C. and Zelazny, L. W., 1986, Effect of sequence in extraction of trace metals from soils. *Soil Science Society of America Journal*, 50, 598-601.
- Pin, C., Zalduendi, J. F. S., 1997, Sequential separation of light rare earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. *Analytical Chimica Acta*, 339, 79-89.
- Plater, A.J., Ivanovich, M., and Douglas, R.E., 1992, Uranium series disequilibrium in river sediments and waters: the significance of anomalous activity ratios. *Applied Geochemistry*, 7, 101-110.
- Poppe, L. J., Paskevich, V. F., Hathaway, J. C., and Blackwood, D. S., 2001, A laboratory manual for X-Ray powder diffraction: USGS Open-File Report 01-041, <http://pubs.usgs.gov/openfile/of01-041/index.htm>
- Schultz, M. K., Burnett, W. C., and Inn, K. G. W., 1998, Evaluation of a Sequential Extraction Method for Determining Actinide Fractionation in Soils and Sediments. *Journal of Environmental Radioactivity*, 40, 155-174.
- Palmer, M. R., and Edmond, J. M., 1993. Uranium in river water. *Geochimica et Cosmochimica Acta*, 57, 4947 – 4955.
- Prytulak, J., Elliott, T., Hoffmann, D.L., and Coath, C.D., 2008, Assessment of USGS BCR-2 as a Reference Material for Silicate Rock U-Pa Disequilibrium Measurements. *Geostandards and Geoanalytical Research*, 32, 55-63.
- Rauret, G., Extraction procedure for the determination of heavy metals in contaminated soil and sediments. *Talanta*, 46, 449-455.
- Rosholt, J., 1982, Mobilization and weathering, *in* Ivanovich, M., and Harmon, R. S., eds., *Uranium-series disequilibrium: Application to environmental problems*. Oxford, Oxford Sciences Publications, pp. 167-180.
- Scott, M. R., 1968, Thorium and uranium concentrations and isotope ratios in river sediments. *Earth and Planetary Science Letters*, 4, 245-252.
- Sims, K.W.W., Gill, J.B., Dosseto, A., Hoffmann, D.L., Lundstrom, C.C., Williams, R.W., Ball, L., Tollstrup, D., Turner, S., Prytulak, J., Glessner, J.J.G., Standish, J.J., and Elliott, T., 2008, An Inter-Laboratory Assessment of the Thorium Isotopic Composition of Synthetic and Rock Reference Materials. *Geostandards and Geoanalytical Research*, 32, 65-91.
- Suresh, P.O., Dosseto, A., Hesse, P.P., and Handley, H.K, 2013, Soil formation rates determined from uranium-series disequilibria in soil profiles from south-eastern Australian highlands. *Earth and Planetary Science Letters*, 379, 26-37.
- Suresh, P.O., Dosseto, A., and Hesse, P., 2010, Links between Catchment Erosion and Climate Investigated with Uranium Series Isotopes. *ASEG Extended Abstracts*, 2010, 1-3.

- Testa, C., Desideri, D., Guerra, F., Meli, M. A., and Roselli, C., 1999, Concentration and speciation of plutonium, americium, uranium, thorium, potassium and ¹³⁷Cs in a Venice canal sediment sample. *Czechoslovak Journal of Physics*, 49, 649-655.
- Townsend, F. N., 1997, Aeolian additions to the soils of the South Easter Australian Highlands. Unpublished Honours Thesis, School of Earth Sciences, Macquarie University, Sydney.
- Turkowsky, C., 1969, Electron-microscopic observation of artificially produced alpha-recoil tracks in albite. *Earth and Planetary Science Letters*, 5, 492-497.
- Turner, S., Beier, C., Niu, Y., and Cock, C., 2011, U-Th-Ra disequilibria and the extent of off-axis volcanism across the East Pacific Rise at 9° 30' N, 10° 30' N and 11° 20' N. *Geochemistry Geophysics Geosystems*, 12, 1-18.
- Turner, S., Calsteren, P.V., Vigier, N., and Thomas, L., 2001, Determination of thorium and uranium isotope ratios in low-concentration geological materials using a fixed multi-collector-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 16, 612-615.
- Vigier, N., Bourdon, B., Turner, S. and Allegre, C. J., 2001, Erosion timescales derived from U-decay series measurements in rivers. *Earth and Planetary Science Letters*, 193, 549-563.
- Vigier, N., and Bourdon, B., 2011, Constraining Rates of Chemical and Physical Erosion Using U-Series Radionuclides, In: Baskaran, M., (Ed.), *Handbook of Environmental Isotope Geochemistry*, Springer Berlin Heidelberg, pp. 553-571.
- Welch, S. A., and Ullman, W. J., 1993, The effect of organic acids on plagioclase dissolution and stoichiometry. *Geochimica et Cosmochimica Acta*, 57, 2725- 2736.
- Williams, R.W., Collerson, K.D., Gill, J.B., and Deniel, C., 1992, High Th/U ratios in subcontinental lithospheric mantle: mass spectrometric measurement of Th isotopes in Gaussberg lamproites. *Earth and Planetary Science Letters*, 111, 257-268.

Tables

Table 1. The leaching and clay separation procedure.

Leached fraction	Reagents	Process
1) Exchangeable/adsorbed/organics	Sodium hypochlorite at pH 7.5 (15 ml/g of sample)	Add reagent to the sample. Heat in the oven at 98°C for 30 minutes. Centrifuge at 7000 rpm for 15 minutes then discard the supernatant. Repeat these steps, add 10 ml ultra-pure water and centrifuge to rinse
2) Carbonates	1 M sodium acetate, adjusted to pH 4 with acetic acid (10 ml/g of sample)	Add reagent to the sample. Agitate at room temperature for 2 hours using a rotary mixer. Centrifuge at 7000 rpm for 15 minutes and discard supernatant. Repeat these steps. Afterwards add 10 ml ultra-pure water, centrifuge at 7000 rpm for 15 minutes then discard the supernatant.
3) Amorphous and crystalline Fe-Mn oxides	0.04 M hydroxylamine hydrochloride (10 ml/g of sample)	Add reagent to the sample. Agitate at room temperature for 5 hours, centrifuge at 7000 rpm for 15 minutes, discard supernatant, add 10 ml Milli-Q water, centrifuge at 7000 rpm for 15 minutes then discard the supernatant.
4) Clay	5% sodium hexa meta phosphate solution, filtered at 0.45µm, 50 ml	Add reagent to the sample. Ultrasonicate at 190 W for 20 s. Agitate overnight. Centrifuge at 1500 rpm for 34 seconds and break-stop the centrifuge in 13 seconds to avoid resettling of clay. Discard supernatant, and repeat centrifugation step with Milli-Q water until the supernatant is clear.

643 Table 2. U and Th concentrations and isotopic data, mineralogy and particle size data of the soil aliquots.

Sample name	Phase extraction steps performed	Th (ppm)*	U (ppm)*	(²³⁴ U/ ²³⁸ U)*	(²³⁰ Th/ ²³⁸ U)*	Quartz	Albite	Microcline	Modal diameter (µm)	< 2 µm fraction (% by wt.)
FLU	Unleached	13.63±0.03	3.968±0.006	0.998±0.002	0.967±0.004	69.3	16.9	13.7	30.7	10.8
FL1	Removed exchangeable, adsorbed and organic material	14.62±0.03	3.675±0.005	0.987±0.002	0.990±0.008	70.8	15.8	13.4		
FL2	Removed exchangeable, adsorbed and organic materials and carbonates	11.66±0.02	3.688±0.005	0.991±0.002	0.958±0.005	70.4	17.5	12.1		
FL3	Removed exchangeable, adsorbed and organic materials, carbonates and amorphous and crystalline Fe-Mn oxides	12.76±0.03	3.932±0.006	0.983±0.002	0.944±0.005	70.9	17.5	11.6		
FL4	Removed exchangeable, adsorbed and organic materials, carbonates, amorphous and crystalline Fe-Mn oxides, and the clay fraction	12.10±0.02	3.126±0.005	0.945±0.002	0.932±0.004	69.1	16.8	14.1	32.7	5.2
FLC	Only clay fraction is removed	12.97±0.02	3.091±0.005	0.940±0.002	0.938±0.005	69.4	17.1	13.5	30.5	4.9

644 *Internal analytical errors of U-series data are 2σ

Table 3. U and Th concentrations and activity ratios of leached and unleached aliquots of TML-3 and BCR-2 rock standards.

Sample	Leached?	Th (ppm)*	U (ppm)*	(²³⁴ U/ ²³⁸ U)*	(²³⁰ Th/ ²³⁸ U)*
TML-3					
T1	No	29.15±0.12	10.34±0.03	0.992±0.003	0.998±0.007
T2	No	29.41±0.01	10.53±0.02	0.994±0.002	0.998±0.007
Mean		29.28±0.12	10.44±0.04	0.993±0.003	0.993±0.009
TL1	Yes	27.57±0.13	9.76±0.02	1.004±0.003	1.004±0.007
TL2	Yes	25.18±0.06	8.94±0.02	1.022±0.002	1.031±0.005
BCR-2					
B1	No	5.513±0.009	1.612±0.001	1.003±0.002	0.984±0.005
B2	No	5.527±0.007	1.637±0.001	0.996±0.001	0.973±0.005
Mean		5.52±0.01	1.624±0.001	1.000±0.002	0.979±0.007
BL1	Yes	5.517±0.008	1.503±0.001	1.007±0.001	1.016±0.004
BL2	Yes	4.573±0.01	2.989±0.005	1.008±0.002	0.451±0.003
From Sims et al. (2008)					
TML-3		30.19±0.64	10.70±0.37	1.000±0.004	0.998±0.015
BCR-2		5.86±0.08	1.69±0.03	1.001±0.005	1.001±0.011

*Internal analytical uncertainties are 2σ.

Figure Captions

Figure 1. Concentration of U and Th in rock standards a) TML-3 and b) BCR-2. Open symbols represent the unleached aliquots and filled symbols represent leached aliquots. Internal analytical errors (2σ) are smaller than the symbol size for most samples. Diamond symbols represent the interlaboratory averaged values reported by Sims et al. (2008). The associated error bars show 2 standard deviation of the individual laboratory values ($n = 35$ for TML-3 and 20 for BCR-2).

Figure 2. Activity ratios of U-series isotopes of a) TML-3 and b) BCR-2 rock standards. Open symbols represents unleached aliquots and filled symbols represent leached aliquots. Internal analytical errors are 2σ . Diamonds represent averaged interlaboratory values ($n = 35$ for TML-3 and $n = 20$ for BCR-2) with 2 standard deviation error bars (Sims et al. 2008).

Figure 3. SEM images of the unleached (FLU) and fully leached, including separation of the clay-sized fraction (FL4) aliquots.

Figure 4. Quantitative mineralogy of leached and unleached aliquots of the soil sample. The labels on the x-axis follow the phase extraction steps for sequential leaching and clay removal outlined in Table 2.

Figure 5. Concentration of U and Th in leached and unleached aliquots of the soil sample. The labels on the x-axis follow the phase extraction steps for sequential leaching and clay removal outlined in Table 2. 2σ internal analytical errors (shown) are similar to the symbol size.

Figure 6. U-series activity ratios of leached and unleached aliquots of soil sample. The labels on the x-axis follow the phase extraction steps detailed in Table 2. Internal analytical errors (2σ) are shown.

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

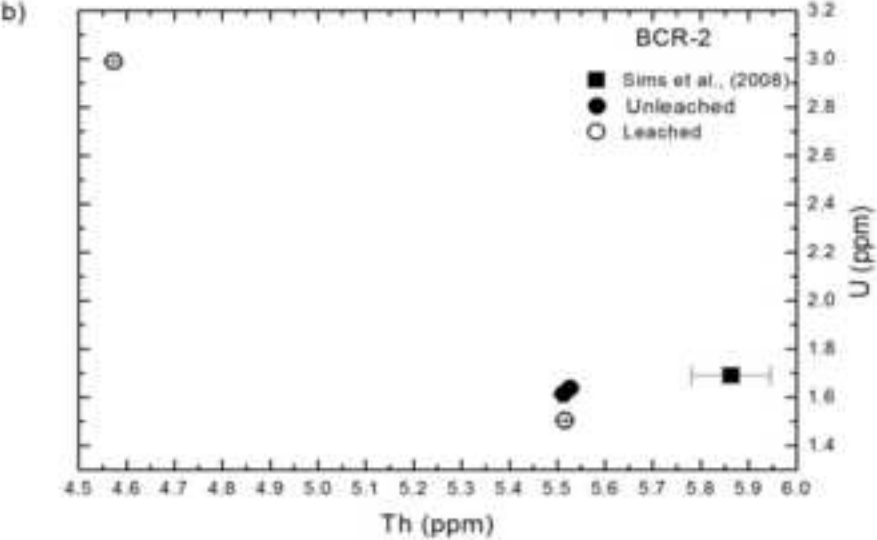
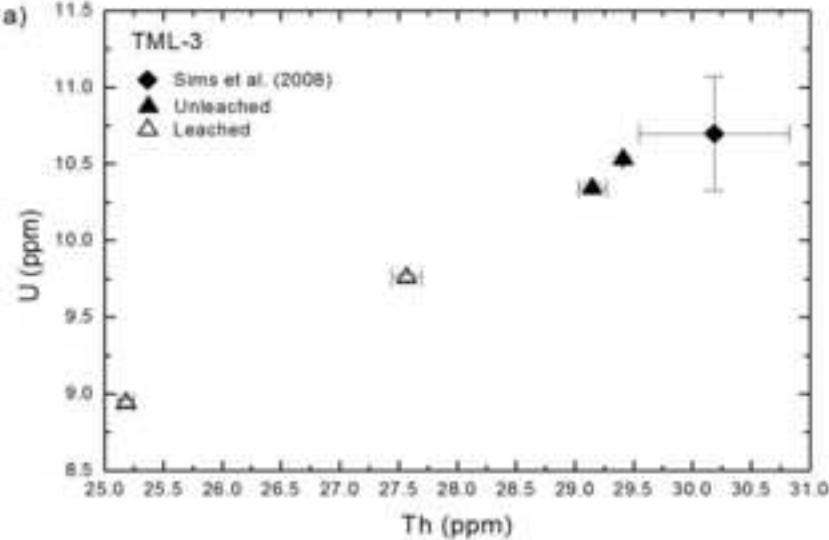


Figure 2
[Click here to download high resolution image](#)

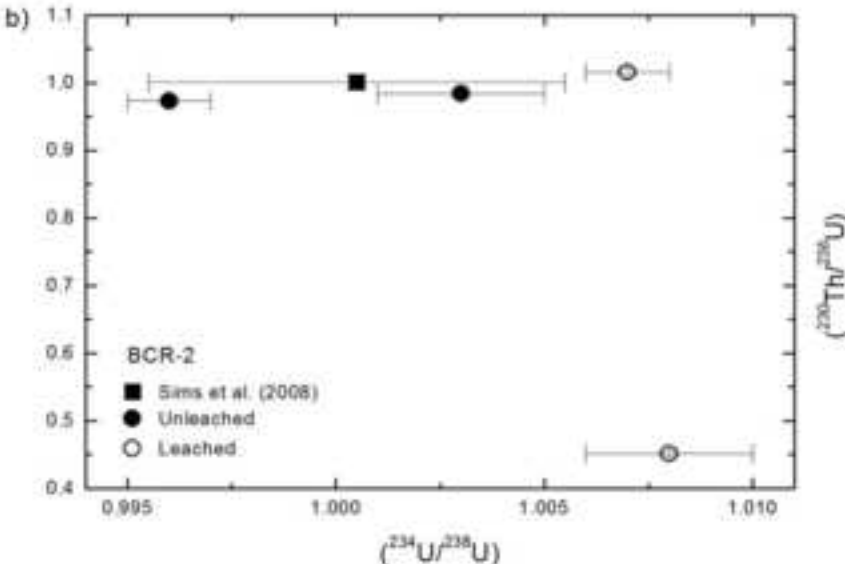
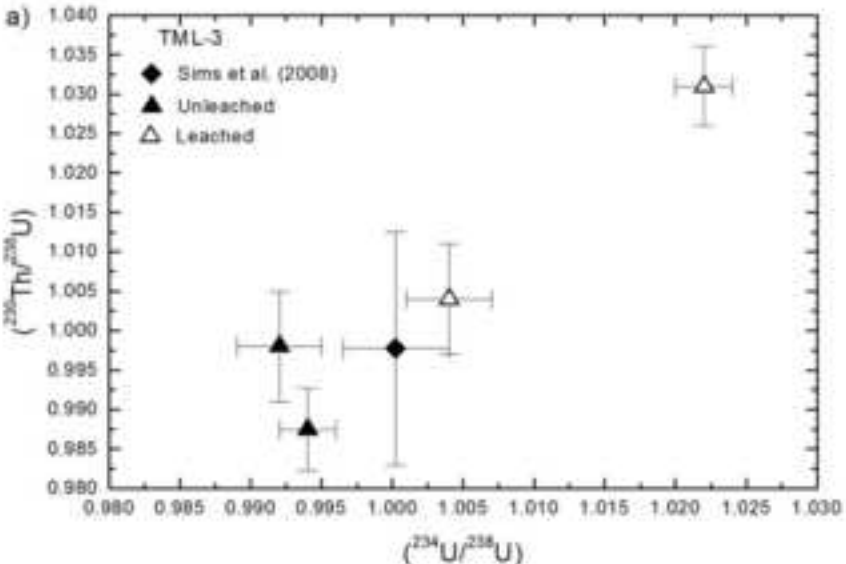


Figure 3
[Click here to download high resolution image](#)

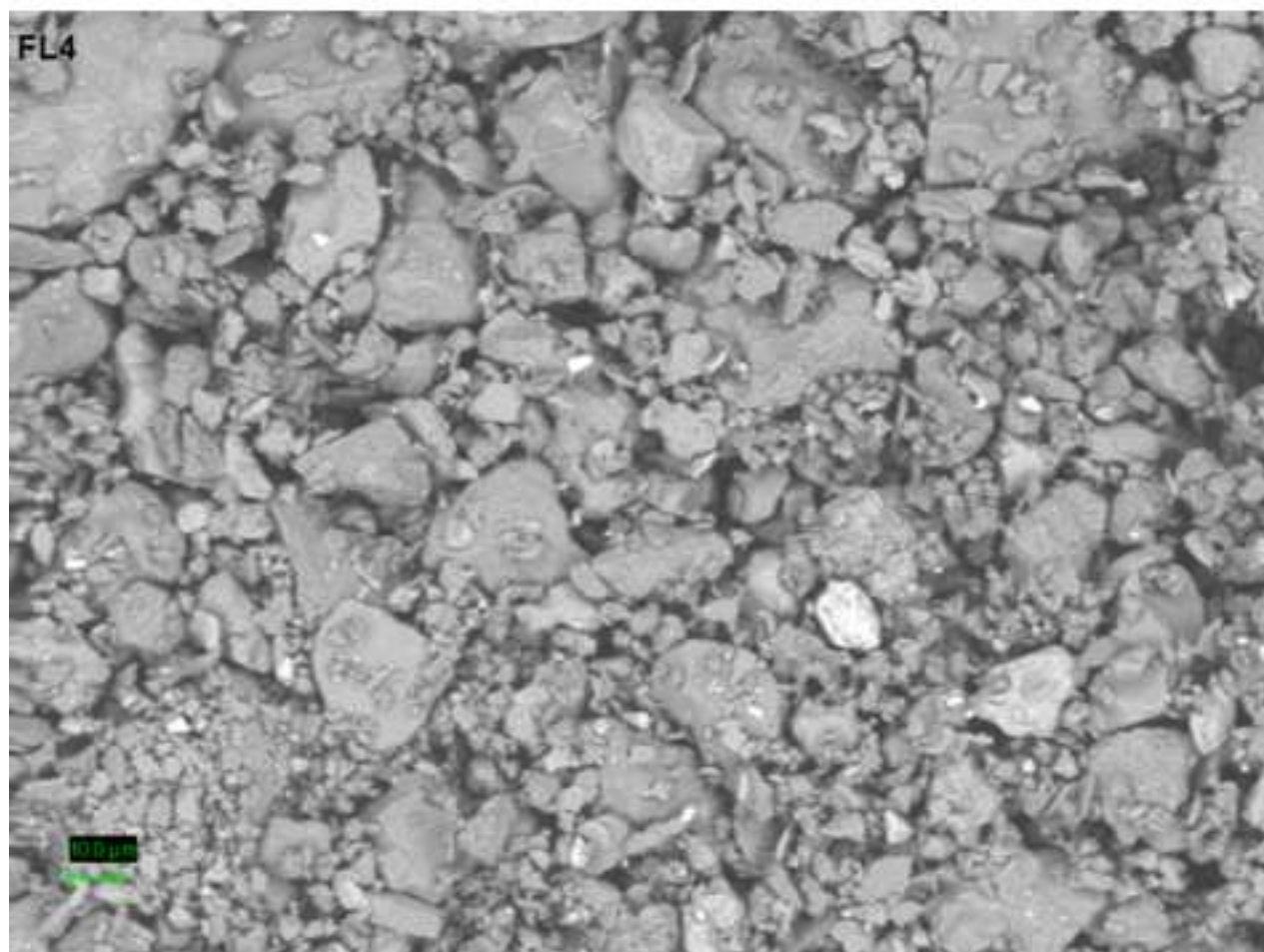
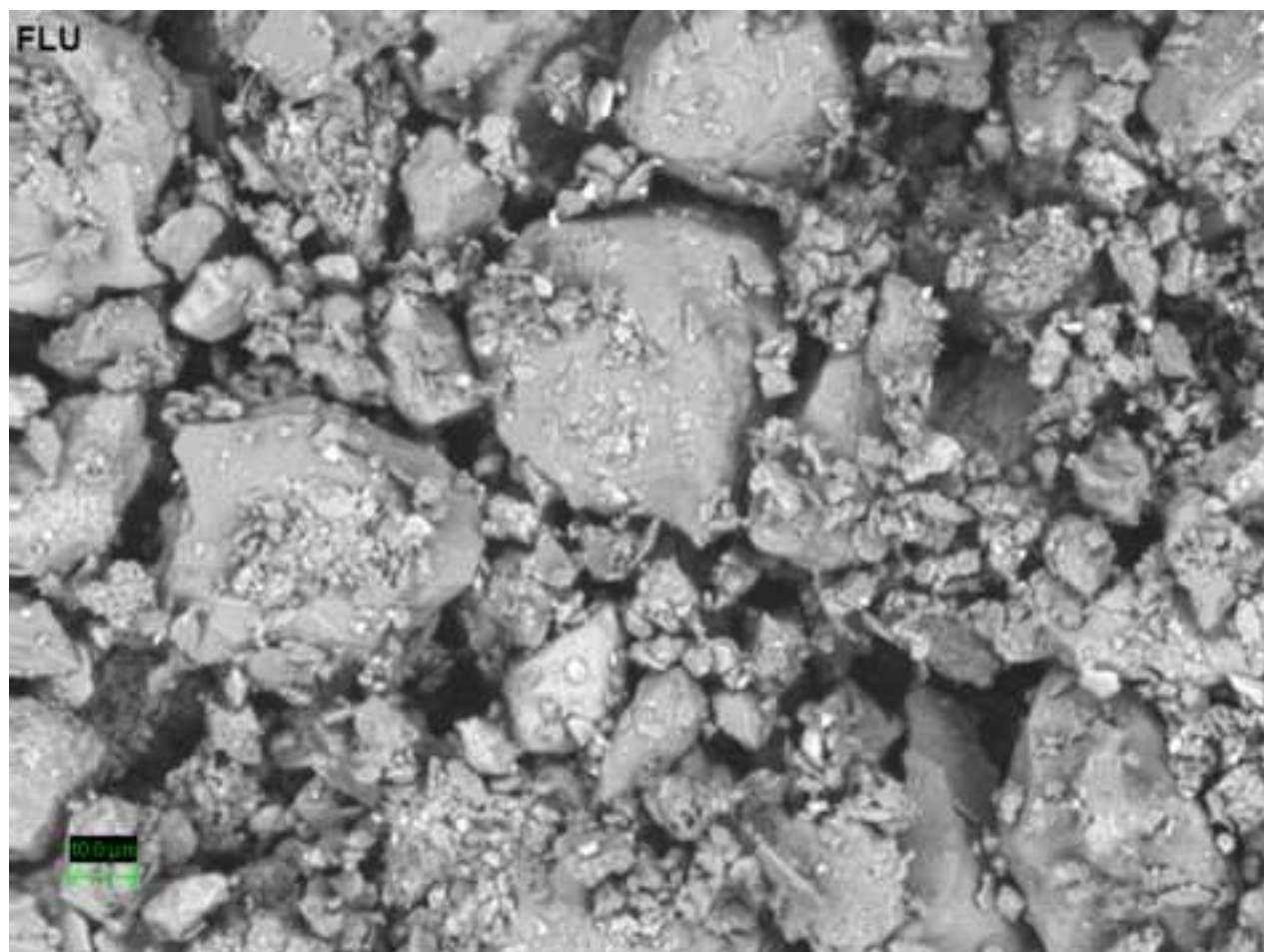


Figure 4

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

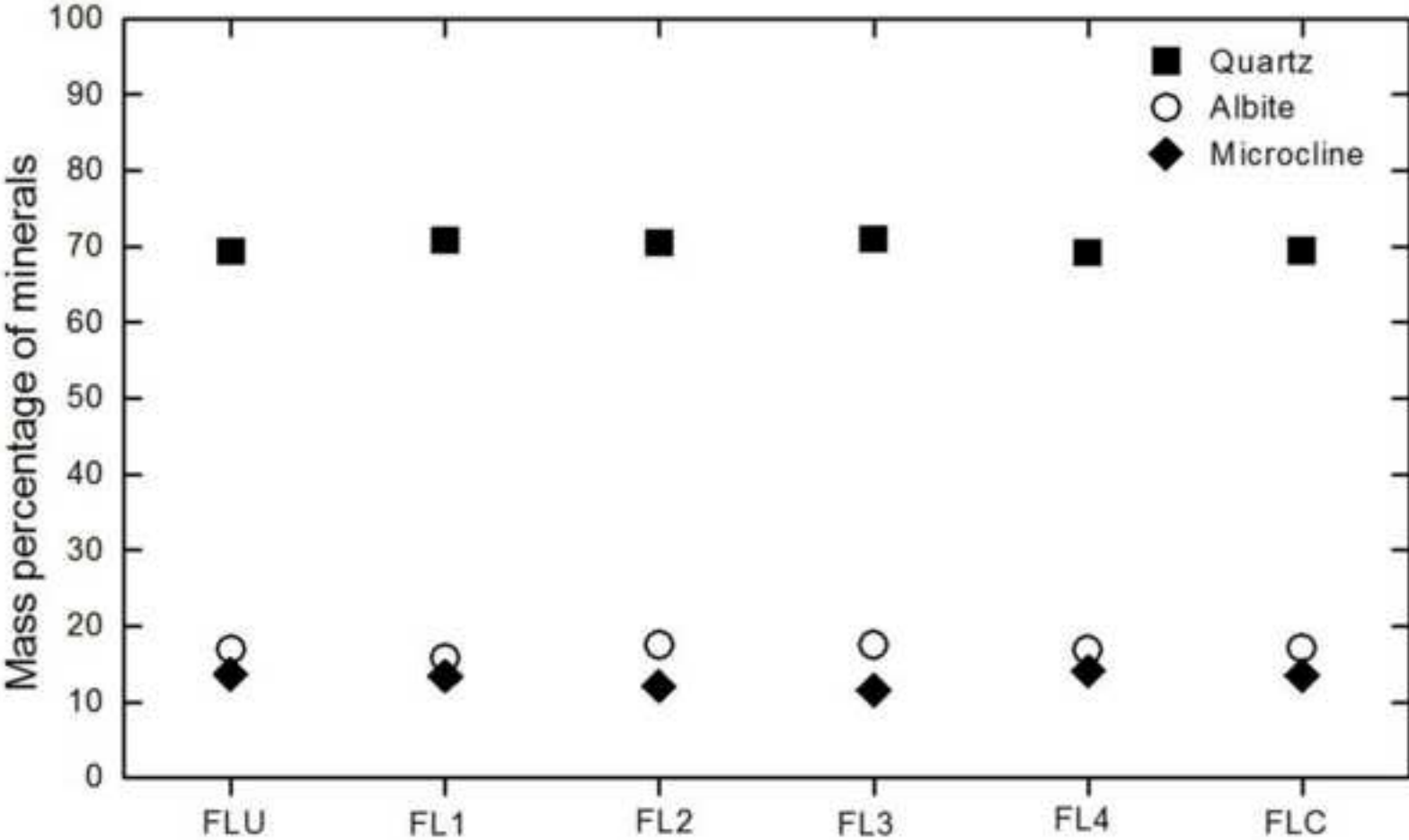


Figure 5
[Click here to download high resolution image](#)

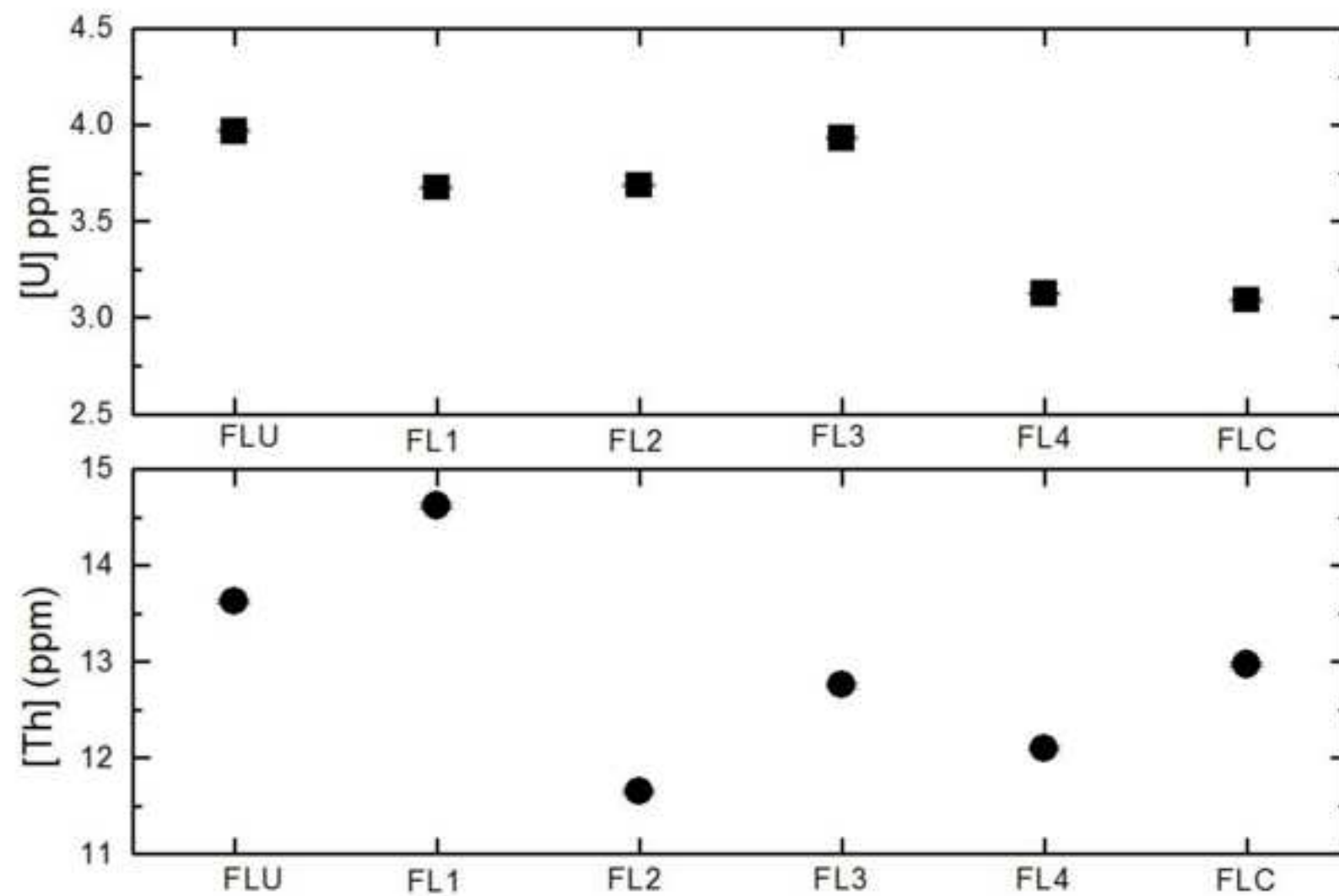


Figure 6
[Click here to download high resolution image](#)

