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

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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

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

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26 Abstract

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

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55 **Keywords**

56 Sequential extraction, U-series, sediments, clay separation

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58 1. Introduction

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

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87 The recoil length for the high energy alpha decay of ^{238}U is ~30 nm in most silicate minerals
88 (Hashimoto et al., 1985; Kigoshi, 1971; Turkowsky, 1969) and therefore this fractionation is
89 only measurable in grains of a few tens of micrometers or less. The measured ^{234}U - ^{238}U
90 disequilibrium can be used to estimate the formation age (comminution age) of the grains
91 following the comminution approach of DePaolo et al. (2006). This approach has been used
92 to determine rates of soil formation and timescales of sediment transport and their
93 relationships to past climate changes (Dosseto et al., 2010; Lee et al., 2010; Suresh et al.,
94 2010; DePaolo et al., 2006).

95 The approaches discussed above are based theoretically on the evolution of U-series
96 isotopes in primary mineral grains since the onset of bedrock weathering, assuming that these
97 isotopes are in secular equilibrium prior to weathering, i.e., that the bedrock is older than 1
98 Ma. However, several previous studies (e.g., Suresh et al., 2013; Dosseto et al., 2012, 2008,
99 2006; Dequincey et al., 2002) have analysed bulk soils and/or sediments, which are complex
100 mixtures of primary minerals, secondary phases and organic materials. Separation of primary
101 minerals from the bulk material for U-series analysis is expected to significantly improve the
102 accuracy of the results obtained from the approaches described above. Efforts have been
103 made to separate primary minerals for the comminution age approach using U isotopes by
104 Dosseto et al. (2010), Lee et al. (2010) and Suresh et al. (2010). However, the effect of the
105 leaching procedure and separation of clay-sized fraction on the U-series isotopes of the
106 primary minerals still needs to be tested.

107 In order to test the reliability and examine the effects on nuclide activity ratios and
108 elemental concentrations of phase extraction procedures proposed here to isolate the primary
109 mineral grains of soil/sediments, we have carried out sequential leaching of soil sample
110 aliquots using a procedure adopted and slightly modified from Schultz et al. (1998) to remove
111 exchangeable and adsorbed fractions, organic materials, carbonates, and amorphous and
112 crystalline Fe-Mn oxides (Table 1). We have added an additional step to physically remove
113 the clay-sized particles by centrifugation (discussed in detail below). The residues from each
114 step of the sequence were analysed for mineralogy, U and Th elemental and isotopic
115 composition and particle size distribution to assess the effects of the removal of the different
116 phases. In addition, powdered standard rock samples were subjected to the same sequential
117 leaching and clay-size fraction removal procedure to assess whether the procedure induces
118 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 M Ω .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 $\geq 99\%$ 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 $<53 \mu\text{m}$ 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

151 supernatant was discarded using a pipette. The material was then rinsed twice with 10 ml of
152 18.2 MΩ.cm Milli-Q water, followed by centrifugation at 7000 rpm for 15 minutes and then
153 careful removal of the supernatant using a pipette. To obtain leached material representative
154 of each step of the leaching procedure sequential leaching was performed on four aliquots
155 (FL1-FL4) for which the leaching stages carried out for each sample are detailed in Table 2.
156 Another aliquot of starting material, FLC, (Table 2) was not chemically leached but had the
157 clay-sized fraction removed by centrifugation. The final aliquot did not undergo any stage of
158 the sequential extraction procedure prior to U-series analysis.

159 The order of extraction of the phases within the procedure is important for the
160 effectiveness of the method (Miller et al., 1986; Shultz et al., 1998). The order of phase
161 extraction used in this study is based on Shultz et al. (1998) and is given in Table 1. Schultz
162 et al. (1998) suggest extraction of the organic fraction immediately after the extraction of the
163 exchangeable fraction, as the thin organic coating on the grains can inhibit the action of
164 reagents used to remove other phases, if performed before organic removal. Schultz et al.
165 (1998) reported that ~ 50% of exchangeable uranium is re-adsorbed when MgCl₂ is used for
166 extraction of exchangeable phases, and therefore that reagent was not used here. We
167 performed removal of exchangeable, adsorbed and organic phases together, using a solution
168 of NaOCl at pH 7.5. An electrolyte prepared from a salt of a strong acid and base or a weak
169 acid and base at pH ~7 can be used for removal of exchangeable fraction from soil (Rauret,
170 1998). The weak complexing ability of Cl⁻ ions in the solution will be sufficient to dissolve
171 the heavy metals weakly bound to the surface of the soil grains (Gleyzes et al., 2002). The
172 use of NaOCl causes re-adsorption of uranium during leaching, but the oxidising nature of
173 NaOCl in the solution is expected to convert the reduced form of uranium to the more soluble
174 oxidised form (Duff et al., 1998). The removal of the adsorbed, exchangeable and organic
175 fractions was accomplished using a solution of 6-14% sodium hypochlorite (15 ml per gram
176 of sample) adjusted to pH 7.5 with 9 M HCl (Table 1). The mixture of the sample and the
177 reagent was heated at 90 °C for 30 minutes. This step was repeated to ensure complete
178 removal of organic matter. The carbonate fraction was removed by treating the sample with a
179 1 M solution of sodium acetate, adjusted to pH 4 with acetic acid (Table 1). The mass ratio of
180 reagent to reactant was 10:1. The mixture was agitated for two hours on a Ratek roller mixer
181 at 30 rpm. This step was repeated twice to ensure complete removal of carbonates.
182 Amorphous and crystalline Fe and Mn oxides were then removed from the sample with a
183 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

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

219 Approximately 100 mg of each sample for uranium-series analysis was spiked with ~
220 30 mg of ^{236}U - ^{229}Th tracer solution and then digested using a mixture of HCl, HNO₃, HF and
221 HClO₄. The samples were left at room temperature for 30 minutes for reaction in closed
222 Teflon beakers and then heated at 130 °C overnight. Sample – tracer equilibration starts
223 immediately during the reaction and will continue throughout the procedure. The mixture
224 was dried at 100 °C for ~ 5 hours and then dried down at 200 °C. The samples were then
225 taken up in 7 M HNO₃ in acid-washed 15 ml centrifuge tubes and centrifuged at 4000 rpm for
226 15 minutes to check that the sample had digested fully. If not, the residue was redigested and
227 added to the solution. This solution was then loaded on chromatographic columns containing
228 AG1X8 anionic resin for the separation of U and Th (Sims et al. 2008; Dosseto et al. 2006).
229 U and Th isotopic analyses were performed using a Nu instrument MC-ICPMS, following the
230 method detailed in (Sims et al. 2008). The U analyses were bracketed with CRM U010
231 isotopic standard. CRM U005-A standard was analysed as an unknown to carry out linear
232 drift correction and to check the normalization of the U isotope measurements of the sample.
233 For Th, all samples were bracketed with the OU Th ‘U’ isotopic reference material for linear
234 drift correction (Sims et al., 2008). The UCSC Th ‘A’ standard was analysed as an unknown.
235 The values of standards measured as unknowns were within 3 ‰ of the recommended values
236 (Sims et al., 2008). The procedural blank for Th was 70 pg and for U it was 20 pg. An
237 unleached TML-3 rock standard was analysed to measure accuracy, which was 1.1% for Th
238 concentration, 0.06% for U concentration, 0.6% for ($^{234}\text{U}/^{238}\text{U}$) and 0.24% for ($^{230}\text{Th}/^{238}\text{U}$).
239 Reproducibility was measured by replicate analysis of unleached TML-3, which was 0.9%
240 for Th concentration, 1.8% for U concentration, 0.17% for ($^{234}\text{U}/^{238}\text{U}$) and 1% for
241 ($^{230}\text{Th}/^{238}\text{U}$).

243 3. Results

244 3.1. Rock standards

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

248 concentration than TL1 and TL2 which were sequentially leached and had the < 2 μm size
249 fraction removed (here after referred to as ‘leached’) (Fig. 1). The weighted average values
250 for Th and U concentrations in TML-3 from an inter-laboratory study (Sims et al., 2008) are
251 within the range of the values measured here for the unleached samples. The Th
252 concentrations of unleached BCR-2 samples B1 and B2 are ~ 20 % higher than those in the
253 leached aliquots BL1 and BL2. B1 and B2 have U concentrations 1.612 ± 0.001 and $1.637 \pm$
254 0.001 ppm whereas the leached aliquots contain 1.50 ± 0.001 and 2.99 ± 0.005 ppm U
255 respectively. The weighted average values for Th and U concentrations in BCR-2 from an
256 inter-laboratory study (Sims et al., 2008) are 5.86 ± 0.08 ppm and 1.69 ± 0.03 ppm,
257 respectively.

258 The unleached (T1, T2) and one of the leached (TL1) TML-3 aliquots yield
259 ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) close to secular equilibrium and within ~ 8 ‰ deviation from the
260 interlaboratory average TML-3 ratios reported by Sims et al. (2008). The other leached
261 aliquot TL2 yields a ($^{234}\text{U}/^{238}\text{U}$) ratio deviating by 21 ‰ from secular equilibrium ratio (Fig.
262 2a). Both the BCR-2 unleached (B1, B2) and leached aliquots (BL1, BL2) have ($^{234}\text{U}/^{238}\text{U}$)
263 close to secular equilibrium (1.003 for the unleached aliquot; 1.007-1.008 for the leached
264 aliquots). The ($^{230}\text{Th}/^{238}\text{U}$) of the leached aliquot BL2 is significantly different from the
265 expected value of 1. This aliquot contains ~2 times higher concentration of U compared to
266 the other aliquots.

267 3.2. Soil samples

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

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

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

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

292 293 4. Discussion

294 The measurements of U and Th concentrations of the unleached rock standards are
295 within the 2σ acceptable limits of their published values. The Th concentrations of the
296 unleached TML-3 aliquots T1 and T2 are within $\pm 4.43\%$ and U concentrations are within
297 -9.1 and 9.1% from those reported by Sims et al. (2008). For the unleached BCR – 2
298 aliquots, B1 is -1.3% and B2 is $+1.3\%$ compared with the Th concentration values
299 published by Sims et al. (2008), and within 2.5% of each other. U concentrations for B1 and
300 B2 are within -7.7 and 7.7% of that published by Sims et al. (2008) and within 15.5% of
301 each other (Fig. 1).

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

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

315 One of the BCR-2 leached aliquots gave a U concentration 77% higher and Th
316 concentration 22% lower than the interlaboratory value (Sims et al. 2008). The aliquot was
317 re-analyzed and yielded similar concentrations (4.48 ppm Th and 2.87 ppm U) which rules
318 out the possibility of analytical problems during analysis by ICPMS. Such a large deviation
319 from accepted U-Th concentration values could possibly result from incomplete
320 sample/tracer equilibration. Similar problems were reported by Pin and Zalduegui (1997)
321 during processing samples for rare earth elements, U and Th. They attributed the problem to
322 incorporation of some of the elements in the tracer to the early stage intermediates of the
323 reaction between the sample and the reagents, which then were not available for
324 equilibration. Formation of stable complex fluorides during dissolution of samples rich in
325 alkaline earth and/or aluminium may mask the U and Th before a full isotopic exchange
326 between sample and tracer occurs (Pin and Zalduegui, 1997). The $[^{236}\text{U}]/[^{238}\text{U}]$ atomic ratio
327 measured by the mass spectrometer for the problematic leached BCR – 2 sample (4.79×10^{-5})
328 is less than half of that measured for the other leached BCR-2 aliquot (1.0879×10^{-4}) and the
329 unleached aliquot (1.01679×10^{-4}), where the amount of sample digested, amount of tracer
330 added and all other measured atomic ratios are similar. The $[^{229}\text{Th}]/[^{232}\text{Th}]$ atomic ratio for
331 the leached aliquot of BCR-2 sample with lower concentration of elemental Th is 6.493×10^{-5} ,
332 whereas for the other leached aliquot it is 7.607×10^{-5} and for the unleached aliquot it is
333 7.30×10^{-5} , confirming the possibility of an incomplete sample-tracer equilibration, although
334 all the TML-3 and BCR-2 aliquots were processed in a similar manner following tracer
335 addition to the sample. Palmer and Edmond (1993) also reported problems due to poor
336 sample/tracer equilibration during U-Th analysis of water samples.

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

1 343 aliquots (BL2) are within a 2σ deviation of $\sim 33\%$ of the value published by Sims et al.
2 344 (2008). The accepted 2σ precision for ($^{230}\text{Th}/^{238}\text{U}$) measurements in rock standards at
3 345 GEMOC is 2 % (Turner et al., 2011). The very low value of ($^{230}\text{Th}/^{238}\text{U}$) of BL1 is due to
4 346 the anomalously high concentration of U measured in it, most likely due to the poor sample-
5 347 tracer equilibration, as discussed above. When compared to the results of U-series activity
6 348 ratios of TML – 3 and BCR – 2 standards published by Sims et al. (2008), and considering
7 349 the accepted 2σ precisions by Turner et al. (2011), it can be observed that the leaching and
8 350 fine-fraction removal procedure employed to the rock standards does not impart any
9 351 artefactual U-series disequilibrium.

10
11 352 The median particle size of the soil sample does not seem to be affected by the clay-
12 353 size fraction separation step. However, the aliquot subjected to sequential leaching and
13 354 removal of the clay-sized fraction (FL4) showed a small increase (6%, compared to 3%
14 355 reproducibility for this instrument) in the median particle size. The minor change median
15 356 particle size is due to the removal of finer fraction.

16
17 357 The leaching and separation procedure did not affect the relative proportions of the
18 358 primary minerals in the soil sample. XRD analysis did not detect any secondary phases in the
19 359 soil sample (detection limit $\sim 1\%$). The mass percentage of primary minerals in the aliquots of
20 360 all steps of the sequential leaching procedure did not show any significant variation (Fig. 4).
21 361 The implication is that the leaching procedure used here does not cause alteration to the
22 362 relative distribution of primary minerals.

23
24 363 The procedure for the removal of the clay-sized fraction will remove particles $< 2\ \mu\text{m}$,
25 364 regardless of mineralogy. Therefore, even primary minerals within the 0-2 μm size fraction
26 365 will be removed. As the relative distribution of primary minerals in the residue is not affected
27 366 by removal of the $< 2\ \mu\text{m}$ fraction, the primary minerals removed have the same relative
28 367 mineralogical distribution as in the bulk sample. After the clay removal step, half of the < 2
29 368 μm size fraction ($\sim 5\%$ total sample mass) remained in the two aliquots. Townsend (1997)
30 369 observed breaking down of soil grains during ultrasonic probing, which affected the particle
31 370 size distribution. Ultrasonication of the sample during the clay-sized fraction removal step
32 371 may have created smaller grains in excess.

33
34 372 Removal of the exchangeable phases and organic materials resulted in a 7.4 %
35 373 decrease in U concentration, implying that a significant proportion of U is contained in this
36 374 phase. No significant change in U concentration was observed after the sodium acetate/acetic

375 acid leaching step, consistent with the restricted carbonate content (lower than XRD detection
1 376 limits) of the soil. The U concentration increased by 6.6% after removal of Fe and Mn oxides,
2 377 showing that there is little or no U in the removed phase. A similar observation was reported
3 378 by Lee et al. (2004), while leaching soil samples with ammonium acetate. When the leaching
4 379 procedure was complete 0.9% of U was removed from the sample.
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10 380 When the clay-size fraction was subsequently removed from the leached sample, U
11 381 concentration decreased by 17% compared with the previous stage, indicating the presence of
12 382 a large proportion of U in the size fraction below 2 μm . Complete removal of the clay-size
13 383 fraction would therefore result in an even greater loss of U. When sequential leaching was
14 384 complete and clay size fraction was removed, 21 % U had been removed, when compared to
15 385 the starting material. When only the clay-sized fraction was removed from the soil aliquot
16 386 without leaching, 22% of U was lost. This shows that a large fraction of U is held in the clay-
17 387 sized fraction of soil. Lee et al. (2004) and Baeza et al. (1995) also observed increases in the
18 388 concentration of U-series isotopes with decreasing soil grain size. Baeza et al. (1995), using
19 389 an empirical relation connecting surface and volume activities of actinides and their ionic
20 390 size, argued that radionuclides with greatest ionic radii are precluded from incorporating to
21 391 crystal lattices and hence their concentrations in refractory minerals will be proportional to
22 392 specific surface area.
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34 393 The 7.3% increase in Th after removal of the exchangeable and organic fractions may
35 394 be due to little or no presence of Th in these fractions. Blanco et al. (2004) also reported that
36 395 Th was present in less than one percent of the organic and exchangeable fractions extracted
37 396 from soil following the method used by Schultz et al. (1998). During the sodium acetate–
38 397 acetic acid buffer leaching stage 20.2% of the initial Th was removed, indicating the presence
39 398 of a large proportion of Th in this leached fraction. Plater et al. (1992) reported removal of up
40 399 to 8.2 % of Th from river sediments during extraction of carbonate. Testa et al. (1999) also
41 400 reported extraction of ~ 14 % Th when the carbonate fraction was separated from canal
42 401 sediments. Our results show that this leaching step can also leach significant amounts of Th
43 402 even when carbonate minerals are absent or in very low abundance (below XRD detection).
44 403 The sample used here is from an acidic soil profile of pH = 5.5 (Suresh et al., 2013). It is
45 404 known that the presence of organic acids increase the mobility of Th from soil (Chabaux et
46 405 al., 2003). It is possible that the mobilized Th might be readsorbed onto the soil grains of this
47 406 sample, and remobilized during leaching with the sodium acetate – acetic acid buffer. There
48 407 was a 9.5% increase in Th concentration of the residue following the removal of Fe and Mn
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408 oxides, indicating little or no presence of Th in the removed fraction. Blanco et al. (2004)
409 also reported that Th was less than one per cent in the Fe and Mn oxide fractions of soil.
410 When removing the clay-size fraction, the Th concentration decreased by 5.1%, indicating
411 the presence of a significant amount of Th in that fraction.

412 Similarly to U concentration variations, ($^{234}\text{U}/^{238}\text{U}$) vary little over the different steps
413 of the sequential leaching, with a slight increase in ^{234}U depletion throughout the procedure,
414 but show a significant decrease when the $< 2 \mu\text{m}$ fraction is removed. This suggests that the
415 $< 2\mu\text{m}$ fraction has a high ($^{234}\text{U}/^{238}\text{U}$). The ($^{230}\text{Th}/^{238}\text{U}$) shows the same systematic changes,
416 but with a more pronounced increase of the disequilibrium throughout the procedure. The
417 removal of the $< 2\mu\text{m}$ fraction does not seem to significantly decrease further the ($^{230}\text{Th}/^{238}\text{U}$)
418 (compared to FL3 and FLC).

419 The organic and exchangeable fraction of soil may have ($^{234}\text{U}/^{238}\text{U}$) > 1 (Plater et al.,
420 1992, Chabaux et al., 2003, Dosseto et al., 2008). Removal of the organic/exchangeable
421 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
422 residue, and the same is observed here. No significant change in the ($^{234}\text{U}/^{238}\text{U}$) was observed
423 after leaching with sodium acetate/acetic acid buffer, again consistent with insignificant or
424 minor presence of carbonate in the sample. Oxides of Fe and Mn in soil will also be
425 characterised by the ($^{234}\text{U}/^{238}\text{U}$) of the soil pore water they precipitate from, which is
426 expected to be > 1 (Dosseto et al., 2008; Plater et al., 1992). Removal of the Fe and Mn oxide
427 fraction from the soil will therefore, decrease the ($^{234}\text{U}/^{238}\text{U}$) of the residue, which was
428 observed here.

429 The lowest ($^{234}\text{U}/^{238}\text{U}$) in the residue was measured for aliquots that underwent the
430 removal of the clay-sized fraction (FL4 and FLC, Table 2) indicating a higher ($^{234}\text{U}/^{238}\text{U}$) in
431 the removed fraction. Authigenic clays will have the U-isotopic signature of the pore water.
432 Clay minerals formed from the pore water are expected to have ($^{234}\text{U}/^{238}\text{U}$) > 1 , as U will be
433 co-precipitated with clay minerals and/or incorporated into the lattices of clay minerals
434 (Scott, 1968; Mitchell, 1964). However, the soil samples processed here do not have
435 detectable clay minerals; therefore, the clay-sized fraction removed must contain largely
436 primary mineral grains. This fraction has the highest specific surface area in the soil, and may
437 contain the most redistributed uranium from the fluid phase, which is expected to be enriched
438 in ^{234}U due to recoil ejection and preferential leaching (Fleischer, 1982; Kigoshi, 1971).
439 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

440 is observed here. The residual primary minerals after leaching and clay-fraction removal have
441 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.
442 (1992) for the residual minerals obtained after leaching river bottom sediments.

443 The ($^{230}\text{Th}/^{238}\text{U}$) increased significantly when the exchangeable and organic fractions
444 were removed. This suggests that the removed fraction has a very low ($^{230}\text{Th}/^{238}\text{U}$). During
445 sequential leaching of river sediments, Plater et al. (1992) also reported ($^{230}\text{Th}/^{238}\text{U}$) as low as
446 0.723 ± 0.362 in extracted organic matter. When the sodium acetate/acetic acid leaching step
447 was performed, the ($^{230}\text{Th}/^{238}\text{U}$) decreased in the residue, indicating a ratio of > 1 in the
448 removed fraction, which is consistent with the observations reported by Plater et al. (1992),
449 when sediment samples were leached to extract carbonate fraction. They also reported that Fe
450 and Mn oxides in the sediments contained ($^{230}\text{Th}/^{238}\text{U}$) > 2 . Removal of a fraction with a
451 higher ($^{230}\text{Th}/^{238}\text{U}$) than the equilibrium value will leave the residue with a ($^{230}\text{Th}/^{238}\text{U}$) of $<$
452 1 , and the same was observed here. Removing the clay-sized fraction from the residue again
453 increased the ($^{230}\text{Th}/^{238}\text{U}$), indicating that the ratio in the removed fraction is lower than the
454 residue from the previous step.

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

459 5. Conclusions

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

472 leaching needs more investigation. Unaccounted removal of U and/or Th from soil and
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2 473 sediment samples during sequential leaching could lead to erroneous estimation of sediment
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4 474 dynamic timescales using U-series models.
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638 Tables

639 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.

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2 643 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

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38 644 *Internal analytical errors of U-series data are 2σ

645 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.

661 Figure Captions

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2 662 Figure 1. Concentration of U and Th in rock standards a) TML-3 and b) BCR-2. Open
3 663 symbols represent the unleached aliquots and filled symbols represent leached aliquots
4 664 Internal analytical errors (2σ) are smaller than the symbol size for most samples. Diamond
5 665 symbols represent the interlaboratory averaged values reported by Sims et al. (2008). The
6 666 associated error bars show 2 standard deviation of the individual laboratory values ($n = 35$ for
7 667 TML-3 and 20 for BCR-2).

10 668
11 669 Figure 2. Activity ratios of U-series isotopes of a) TML-3 and b) BCR-2 rock standards.
12 670 Open symbols represents unleached aliquots and filled symbols represent leached aliquots.
13 671 Internal analytical errors are 2σ . Diamonds represent averaged interlaboratory values ($n = 35$
14 672 for TML-3 and $n = 20$ for BCR-2) with 2 standard deviation error bars (Sims et al. 2008).

15 673
16 674 Figure 3. SEM images of the unleached (FLU) and fully leached, including separation of the
17 675 clay-sized fraction (FL4) aliquots.

18 676
19 677 Figure 4. Quantitative mineralogy of leached and unleached aliquots of the soil sample. The
20 678 labels on the x-axis follow the phase extraction steps for sequential leaching and clay removal
21 679 outlined in Table 2.

22 680
23 681 Figure 5. Concentration of U and Th in leached and unleached aliquots of the soil sample.
24 682 The labels on the x-axis follow the phase extraction steps for sequential leaching and clay
25 683 removal outlined in Table 2. 2σ internal analytical errors (shown) are similar to the symbol
26 684 size.

27 685
28 686 Figure 6. U-series activity ratios of leached and unleached aliquots of soil sample. The labels
29 687 on the x-axis follow the phase extraction steps detailed in Table 2. Internal analytical errors
30 688 (2σ) are shown.

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Figure 1
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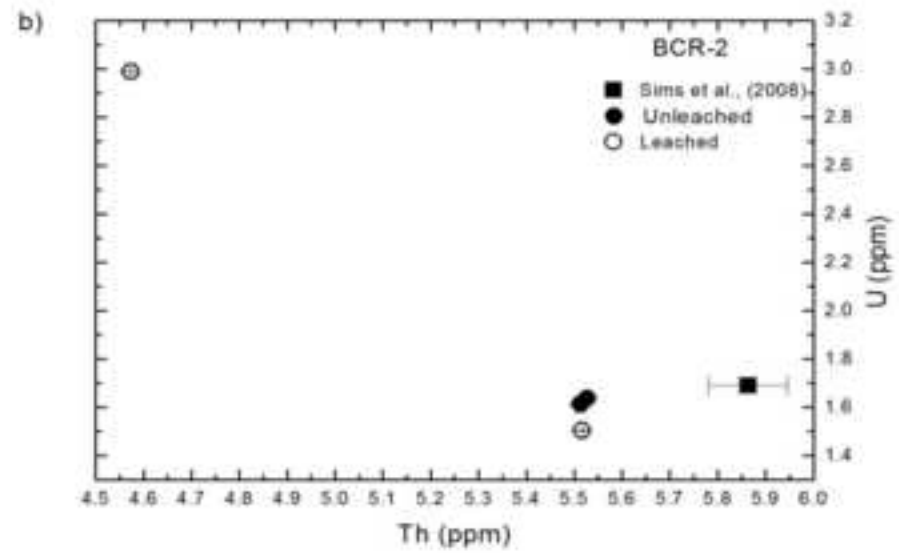
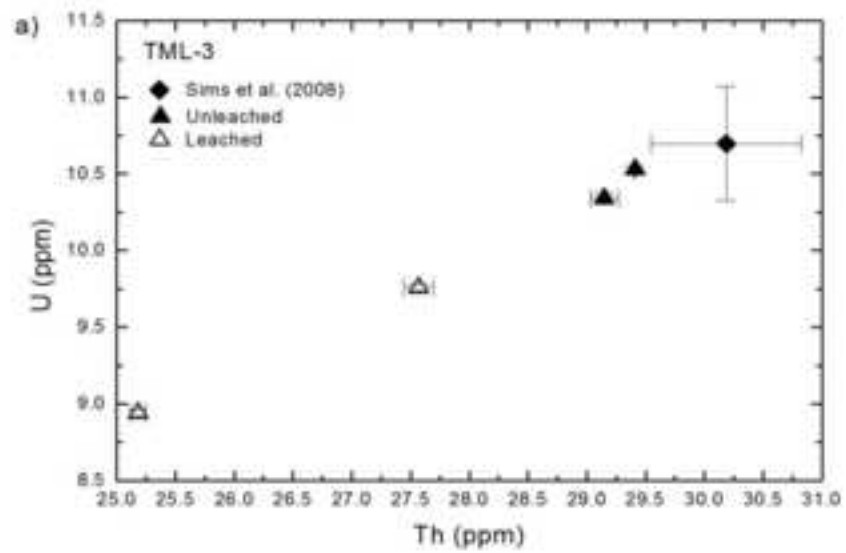


Figure 2
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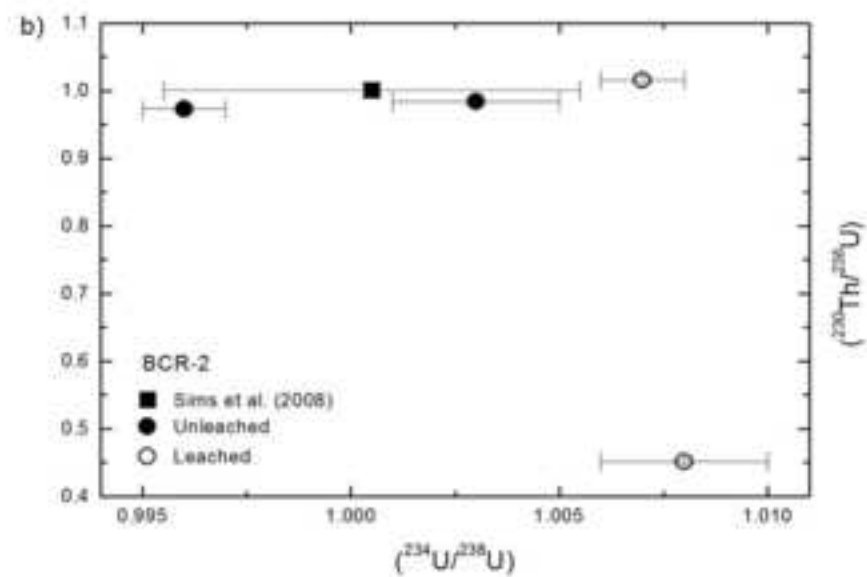
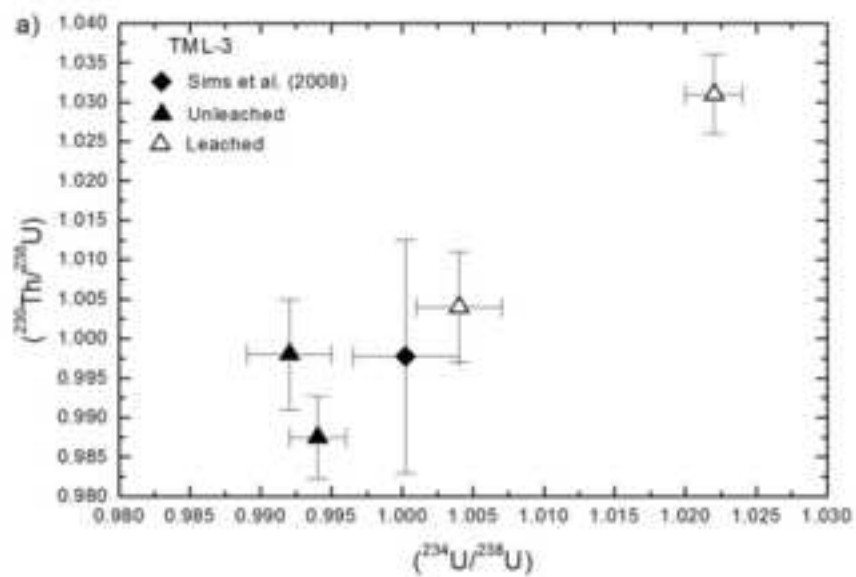


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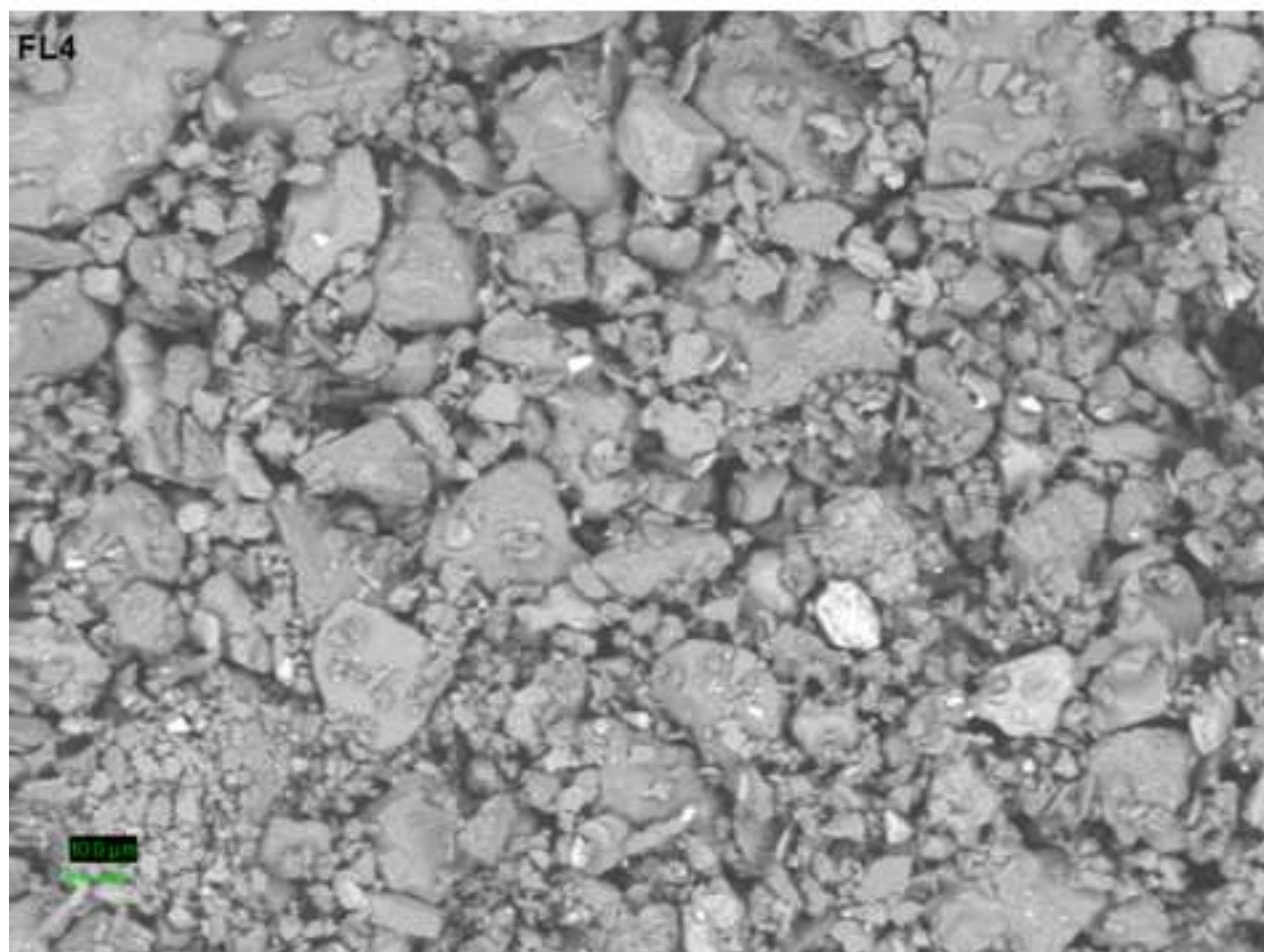
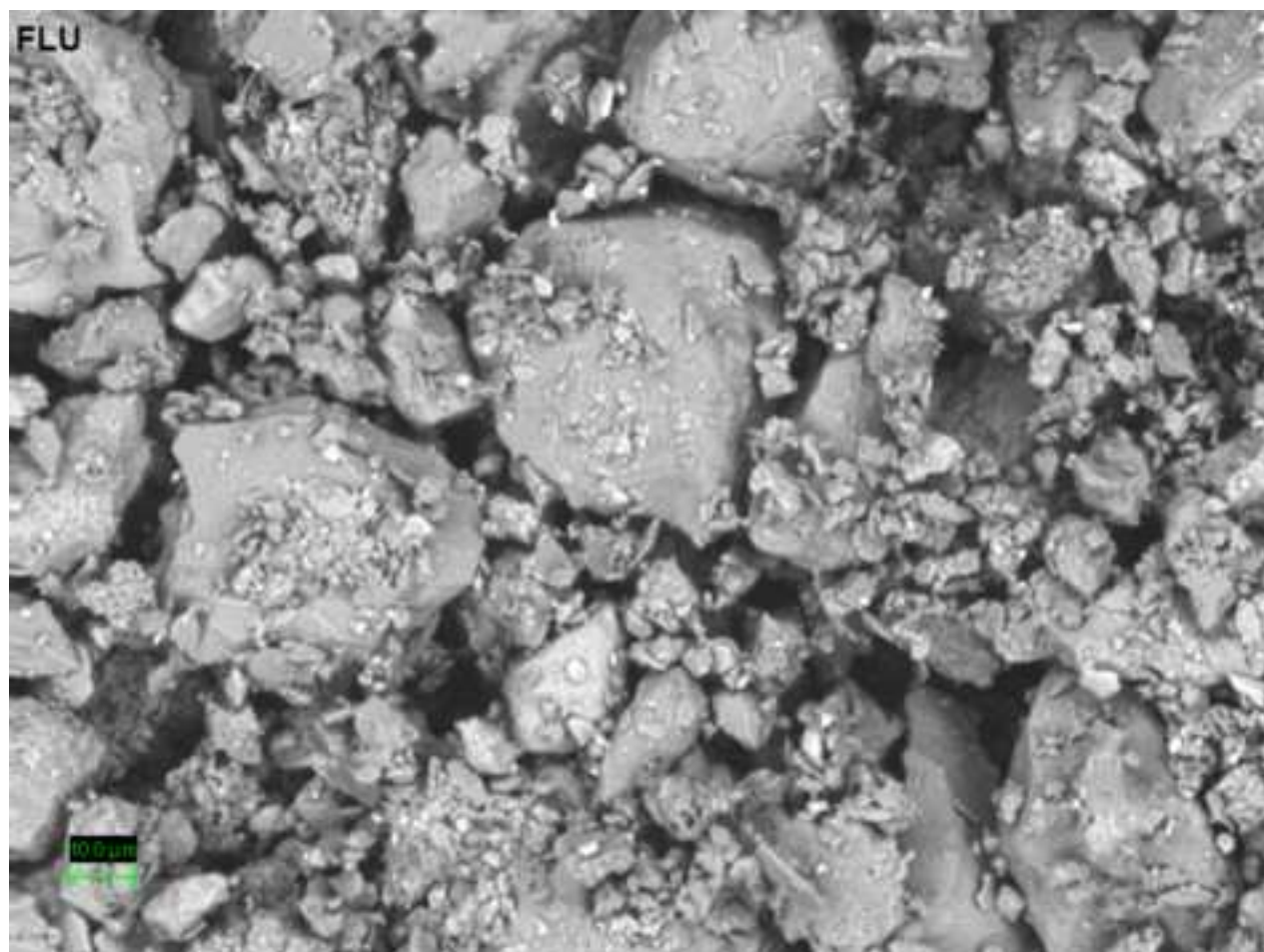


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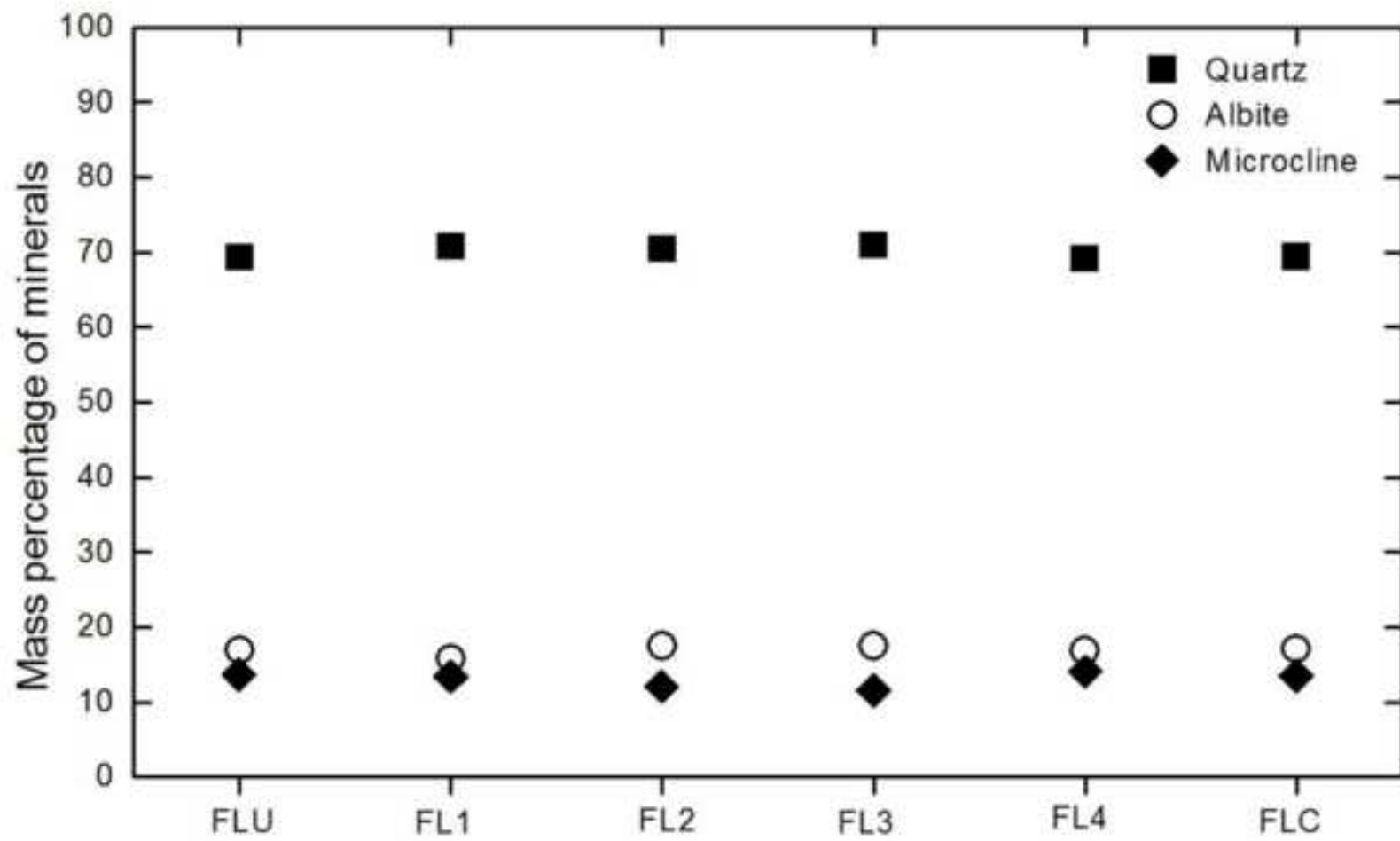


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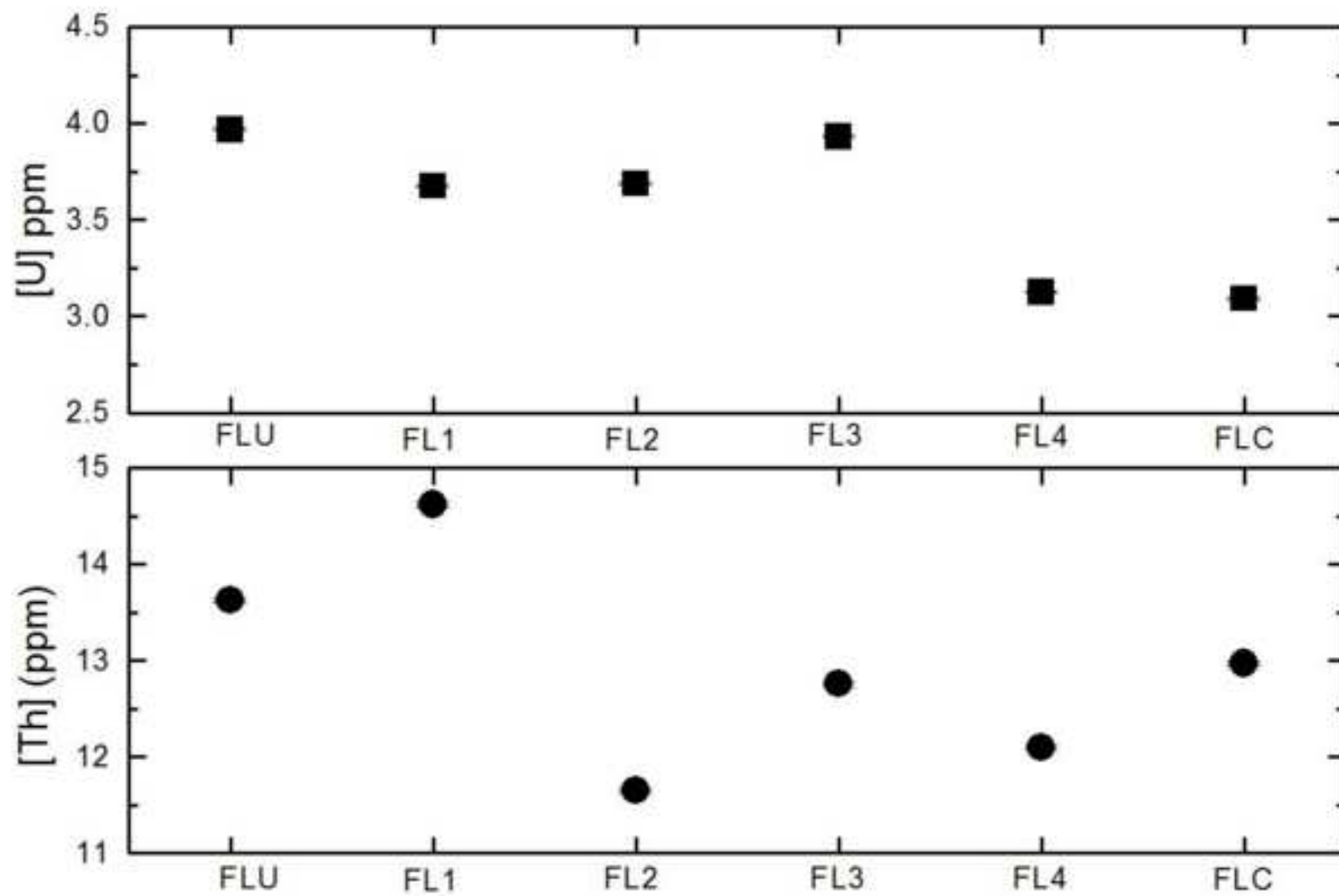


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