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Sample preparation for determination of comminution ages in lacustrine and marine sediments

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Sample preparation for determination of comminution ages in lacustrine and marine sediments

Abstract

The uranium isotope composition (^{234}U and ^{238}U) of detrital matter has become an essential tool for evaluating the response of erosion and catchment dynamics to climate variability on geological time scales. Relative variability of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio can be used as an estimate of the time that has elapsed since physical and chemical weathering has formed grains $< 63\mu\text{m}$, termed comminution age, as a result of ongoing depletion of ^{234}U in detrital matter. However, as non-detrital (authigenic, endogenic) components are commonly enriched in ^{234}U , sequential extraction methods are required to carefully remove any non-detrital matter from the sediments. Herein, we tested different methods, which use similar chemical reactants but differ in terms of applied heat and time. Based on the results, it can be inferred that an ultrasound-assisted approach enables the removal of non-detrital matter from the sediments without alternating the isotope ratio of the detrital grain, and provides a high reproducibility of the ($^{234}\text{U}/^{238}\text{U}$) activity ratios. Moreover, it is the fastest, and thus, most cost effective method tested. Fast and cost-effective treatment methods are a prerequisite for high-resolution studies on long paleoenvironmental records, and thus, these results are fundamental for the further development of U isotope analyses as a tool for the reconstruction of past erosion and catchment dynamics in response to climate variability. Combined U isotopes and gas absorption surface area analyses on two sediment samples from the Mediterranean Sea yield comminution ages up to 5 times older after sample treatment, which highlights the importance of a comprehensive removal of non-detrital matter from the bulk sediment composition. Moreover, gas sorption analysis allowed determining whether a fractal correction for calculation of the recoil fraction should be applied. Precise estimates of the recoil fraction are crucial for calculating the comminution ages, as it governs the loss of ^{234}U from detrital matter. Samples analyzed in this study display Type II isotherms suggesting a non-porous or macroporous surface. Micro- and mesopores, which increase the surface area during gas absorption analyses but do not contribute to the loss of ^{234}U are absent. Thus, a fractal correction to account for micro- and mesopores is not required.

Disciplines

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1 **Sample preparation for determination of comminution ages**
2 **in lacustrine and marine sediments**

3

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13 development, erosion, gas absorption, lake sediment, marine sediment

14

15 **Abstract**

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17 essential tool for evaluating the response of erosion and catchment dynamics to climate
18 variability on geological time scales. Relative variability of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio
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25 heat and time. Based on the results, it can be inferred that an ultrasound-assisted
26 approach enables the removal of non-detrital matter from the sediments without
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28 the ($^{234}\text{U}/^{238}\text{U}$) activity ratios. Moreover, it is the fastest, and thus, most cost effective
29 method tested. Fast and cost-effective treatment methods are a prerequisite for high-
30 resolution studies on long paleoenvironmental records, and thus, these results are
31 fundamental for the further development of U isotope analyses as a tool for the
32 reconstruction of past erosion and catchment dynamics in response to climate
33 variability.

34 Combined U isotopes and gas absorption surface area analyses on two sediment samples
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36 treatment, which highlight the importance of a comprehensive removal of non detrital
37 matter from the bulk sediment composition. Moreover, gas sorption analysis allowed
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39 applied. Precise estimates of the recoil fraction are crucial for calculating the
40 comminution ages, as it governs the loss of ^{234}U from detrital matter. Samples analyzed
41 in this study display Type II isotherms suggesting a non-porous or macroporous surface.
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43 but do not contribute to the loss of ^{234}U are absent. Thus, a fractal correction to account
44 for micro- and mesopores is not required.

45

46 1. Introduction

47 Our ability to reconstruct paleoclimatic conditions by using various proxy data sets have
48 immensely increased over the past decades (e.g. Lang and Wolff, 2011). However,
49 reliable information about past erosional processes in response to environmental and
50 climatic variability are still difficult to obtain on geological time scales (Dosseto and
51 Schaller, 2016). Such information is not only crucial in order to better assess future
52 modifications of soil erosion under scenarios of future climate change, it also provides
53 important insights into the erosion-driven fixation of atmospheric carbon dioxide (CO₂)
54 by silicate weathering (Lee et al., 2010a). One approach to overcome the sparse
55 availability of information about the erosional processes on geological time scales is to
56 use the (²³⁴U/²³⁸U) activity ratio of detrital material in sedimentary deposits to
57 reconstruct changes in catchment erosion (e.g. DePaolo et al., 2006; Lee et al., 2010a;
58 DePaolo et al., 2012; Dosseto and Schaller, 2016). Uranium-234 and ²³⁸U record the time
59 elapsed since parent material was weathered to fine-grained (typically <63µm) regolith
60 (Suresh et al., 2014a), as ²³⁴Uranium is continuously lost from regolith during storage
61 and transport on hillslopes (Dosseto et al., 2008; Ma et al., 2010; Gontier et al., 2015;
62 Suresh et al., 2013; Suresh et al., 2014a,b). Because of the older *weathering age* (Dosseto
63 et al., 2014) or *comminution age* (DePaolo et al., 2006; Lee et al., 2010a) of detrital
64 matter from shallow regolith layers, samples from shallower soil horizons show lower
65 (²³⁴U/²³⁸U) activity ratios than samples from deeper horizons. The (²³⁴U/²³⁸U) activity
66 ratio can be further lowered in sediments if alluvial transport and storage takes longer
67 than a few thousands of years (Chabaux et al., 2006; Dosseto et al., 2006b; Granet et al.,
68 2010; Granet et al., 2007). Thus, when applied to sedimentary deposits, variations in the
69 (²³⁴U/²³⁸U) activity ratio of detrital matter can inform about changes in hillslope erosion
70 and/or alluvial transport. Furthermore, by combining the (²³⁴U/²³⁸U) activity ratio of
71 detrital sediments to measurements of their surface area, the comminution age can be
72 tentatively quantified (DePaolo et al., 2006; Dosseto et al., 2010; Lee et al., 2010a;
73 DePaolo et al., 2012; Handley et al., 2013a,b). More recently, it was shown that a
74 relationship between the (²³⁴U/²³⁸U) activity ratio of alluvial sediments and catchment-
75 wide erosion rates exist, which illustrates the sensitivity of this proxy to erosion
76 processes (Li et al., 2017a).

77 One of the challenges for obtaining useful information from the (²³⁴U/²³⁸U) activity ratio
78 of sedimentary deposits stems from the nature of sediments: they are commonly a

79 complex mixture of detrital minerals, and authigenic and endogenic phases(referred as
80 non-detrital matter from hereon). Thus, treatment methods are required in order to
81 carefully remove any non-detrital matter from the sample without alternating the
82 surface of detrital grains, since loss of ^{234}U occurs within ~ 30 nm of the surface (Martin
83 et al., 2015; Suresh et al., 2014b). Non-detrital matter is commonly characterized by a
84 high ($^{234}\text{U}/^{238}\text{U}$) activity ratio, since it derives its U from solution (e.g. pore water).
85 Uranium radionuclides are in continuous state flux between detrital matter and the pore
86 water by recoil displacement of ^{234}Th and U sorption, resulting in an enrichment in ^{234}U
87 of the aqueous phase (Andersson et al., 2001; Andersson et al., 1998; Paces et al., 2013;
88 Plater et al., 1992; Porcelli et al., 1997). Thus, the ($^{234}\text{U}/^{238}\text{U}$) activity ratio in authigenic
89 and endogenic matter strongly depends on the local hydrologic conditions and may even
90 vary on a seasonal scale (Plater et al., 1992). If non-detrital matter is not removed from
91 the bulk sediment, the ($^{234}\text{U}/^{238}\text{U}$) activity ratios reveal higher values, mistakenly
92 suggesting deep erosion and/or short residence times. Values can even be >1 , in which
93 case no information on erosion and sediment transport can be derived.

94 Extensive studies have been carried out in order to estimate the impact of sequential
95 extraction procedures to remove any non-detrital matter from bulk sediment
96 compositions, such as water soluble and exchangeable fractions, non-detrital calcite,
97 iron/manganese-oxides (Fe/Mn-oxides), and organic matter (e.g. Blanco et al., 2004;
98 Dosseto et al., 2010; Lee et al., 2010a; Suresh et al., 2014b). Most of these studies
99 evaluate and further develop the work of Tessier et al. (1979) and Schultz et al. (1998)
100 and show that a considerable amount of U is removed during sequential extraction, in
101 particular bound to organic matter (Plater et al., 1992; Suresh et al., 2014b). Thus,
102 sequential extraction methods can have a significant impact on the ($^{234}\text{U}/^{238}\text{U}$) activity
103 ratio (Plater et al., 1992), whereby a careful evaluation is required to estimate if these
104 modifications are due to the removal of non-detrital matter, as intended, or due to
105 modifications in ($^{234}\text{U}/^{238}\text{U}$) activity ratios of the residual detrital matter by mineral
106 dissolution. Most comprehensive work has recently been carried out by Martin et al.
107 (2015), suggesting that the methods of Schultz et al. (1998) are most effective. In
108 addition, Martin et al. (2015) introduced a mild hydrofluoric/hydrochloride (HF/HCl)
109 acid etch, which aims to find the lowermost possible ($^{234}\text{U}/^{238}\text{U}$) activity ratio after
110 sample treatment by removing leftover non-detrital matter after sequential extraction.
111 Martin et al. (2015) address mostly soil samples and only to a limited extent marine
112 sediments, and the described method is very time consuming. Applying U isotope

113 analyses on long, continuous paleoclimate archives (such as lacustrine and marine
114 records) covering several glacial-interglacial cycles requires a fast and cost-effective
115 treatment method in order to allow high-resolution studies far back in time.

116 Herein, we evaluate the applicability of the purposed sequential extraction procedure by
117 Martin et al. (2015) on lacustrine deposits from Lake Ohrid (Former Yugoslav Republic
118 of Macedonia (FYROM), Albania), and on marine sediment sequences from the
119 Mediterranean Sea and the Tasman Sea offshore New Zealand. Martin et al. (2015) used
120 a hotplate for treatment steps requiring heat, however, the small contact area between
121 sample vial and hotplate might result in significantly lower sample temperatures as the
122 desired target temperatures. Therefore, we repeat the experiments of Martin et al.
123 (2015) using an oven to achieve the desired target temperatures. We also test the
124 impact of the mild HF/HCl acid etch on our samples. Additionally, we evaluate the
125 sonication-assisted procedure suggested by Väisänen and Kiljunen (2005), which is
126 much faster, and thus, more cost-effective. Finally, we elaborate the impact on the
127 ($^{234}\text{U}/^{238}\text{U}$) activity ratio of a extraction step introduced to remove biogenic silica, which
128 can be abundant in both lacustrine and marine deposits due to the presence of diatom
129 frustules and sponge needles (Cohen, 2003).

130 Sequential extraction methods can have a considerable impact on the surface area of a
131 sediment sample as (1) it removes low-surface-area material such as organic matter
132 (Martin et al., 2015), and (2) it might decrease the roughness of the mineral grains (Li et
133 al., 2017b). A precise knowledge of the surface area properties is crucial for the
134 calculation of comminution ages, as it determines the loss of ^{234}U over time. The surface
135 properties of a sediment sample can be measured by means of gas absorption analyses.
136 We test the impact of the sequential extraction methods on the surface area and the
137 surface roughness by measuring the surface properties of untreated and treated aliquots
138 of the same sample material.

139 **2. Conceptual model**

140 The conceptual model of U isotopes for estimating the comminution age, i.e. the time
141 that has elapsed since physical and chemical weathering has formed grains $<63\mu\text{m}$, is
142 based on the significant fractionation between ^{234}U and ^{238}U in rocks close to the Earth's
143 surface. In geological closed system (such as bedrock), the radioactive daughter nuclide
144 ^{234}U and the parent nuclide ^{238}U are in *secular equilibrium* ($(^{234}\text{U}/^{238}\text{U}) = 1$).

145 Fractionating of ^{234}U becomes significant in grains $<63\mu\text{m}$, which are characterized by a
 146 large surface- to- volume ratio (DePaolo et al., 2006; DePaolo et al., 2012; Martin et al.,
 147 2015). Thereby, the ^{234}U depletion is a result (a) direct recoil of ^{234}Th , an intermediate
 148 product between ^{238}U and ^{234}U , (b) preferential leaching of ^{234}U embedded in the recoil
 149 tracks, and (c) preferential oxidation of ^{234}U compared to ^{238}U (summarized in Dosseto
 150 and Schaller, 2016). The disequilibrium between ^{234}U and ^{238}U enables the calculation of
 151 the comminution age t_{com} (DePaolo et al., 2006):

$$t_{\text{com}} = -\frac{1}{\lambda_{234}} \ln \left[\frac{A_{\text{meas}} - (1 - f_4)}{A_0 - (1 - f_4)} \right] \quad (1)$$

153 where λ_{234} is the ^{234}U decay constant (in yr^{-1}), A_{meas} the measured ($^{234}\text{U}/^{238}\text{U}$) activity
 154 ratio, A_0 the initial ($^{234}\text{U}/^{238}\text{U}$) activity ratio in the bedrock, and f_4 the recoil loss factor.
 155 As the recoil loss factor f_4 is a function of the grain surface area, it can be estimated using
 156 BET gas absorption analyses: :

$$f_4 = \frac{1}{4} LS\rho \quad (2)$$

159 where L is the recoil length of ^{234}Th (30 nm), ρ the density (2.65 g/cm^3), and S the
 160 surface area (m^2/g) as measured by BET analyses (Kigoshi, 1971; Luo et al., 2000). BET
 161 analysis accounts for the surface roughness of detrital grains at the scale of the molecule
 162 diameter of nitrogen (0.354 nm), which is ~ 100 times smaller as the recoil distance L .
 164 Thus, a high surface roughness could result in an overestimation of the recoil loss factor
 165 f_4 (Maher et al., 2006). To account for this difference in scale length, Bourdon et al.
 166 (2009) proposed to write the recoil loss fraction as

$$f_4 = \frac{1}{4} \left[\frac{2^{D-1}}{4-D} \left(\frac{\alpha}{L} \right)^{D-2} \right] LS\rho \quad (3)$$

168 where D is the fractal dimension of the surface and α the size of the absorbate. The
 169 fractal dimension D can be measured by BET analysis, varies between 2 (perfectly
 170 smooth surface) and 3 (maximum surface complexity), and is in essence similar to the
 171 surface roughness of a grain (Bourdon et al., 2009; Dosseto and Schaller, 2016). Because
 172

173 the recoil distance of ^{234}Th is $\sim 30\text{nm}$ in most silicates (Dosseto and Schaller, 2016), the
174 depletion of ^{234}U takes place in the outer rind of a detrital grain, resulting in the
175 expectation of three different domains in fine-grained, sedimentary deposits (Dosseto
176 and Schaller, 2016; Handley et al., 2013a). Domain 1 corresponds to the inner core of a
177 detrital grain, where no loss of ^{234}U occurs. Thus, ^{234}U and ^{238}U are in *secular* equilibrium
178 in Domain 1 matter ($(^{234}\text{U}/^{238}\text{U}) = 1$). Domain 2 encompasses the outer $\sim 50\text{nm}$ of a
179 detrital grain, where recoil of the daughter nuclide ^{234}Th results in loss of ^{234}U , yielding
180 $(^{234}\text{U}/^{238}\text{U})$ activity ratios < 1 . Domain 3 accounts for all non-detrital matter of
181 authigenic and/or endogenic origin (such as organic matter, non-detrital carbonates,
182 authigenic minerals, biogenic silica). Authigenic and endogenic matter commonly exhibit
183 $(^{234}\text{U}/^{238}\text{U})$ activity ratios > 1 as it derived its U from natural waters, which are enriched
184 in ^{234}U due to the recoil effect (Kigoshi, 1971).

185 In order to obtain meaningful information about erosion processes and about
186 comminution ages, any Domain 3 components must be removed from the bulk sediment
187 composition. As Domain 3 material is increasingly removed, the $(^{234}\text{U}/^{238}\text{U})$ activity ratio
188 is expected to decrease continuously (Fig. 1). Sample treatment must not affect the
189 outer, ^{234}U -depleted rim of the detrital grains (Domain 2), otherwise an increase in
190 $(^{234}\text{U}/^{238}\text{U})$ should be observed, eventually reaching *secular equilibrium* if all Domain 2
191 material is removed (Fig. 1). Thus, when evaluating sequential extraction methods, the
192 $(^{234}\text{U}/^{238}\text{U})$ activity ratio can be measured during progress (Fig. 1) with the minimum
193 value representing the optimal treatment (Lee, 2009; Martin et al., 2015, see also Fig. 1).
194 Herein, we follow a similar approach, investigating variations in $(^{234}\text{U}/^{238}\text{U})$ activity
195 ratio at different steps of various sequential extraction methods (Lee, 2009; Martin et al.,
196 2015, Fig. 1)

197 **3. Material**

198 **3.1 Samples**

199 Sediment material from Lake Ohrid, located at the border between FYROM and Albania,
200 has been recovered during a deep drilling campaign in 2013 at the so-called DEEP site
201 ($41^{\circ}02.9'\text{N}$, $020^{\circ}42.9'\text{E}$) in the central part of the lake (see Wagner et al., 2014 for more
202 details). Fine-grained, hemipelagic sediments at the DEEP site can be found down to
203 $\sim 450\text{ m}$ sediment depth. The selected core catcher sample 1B-17H-cc used in this study
204 corresponds to the sediments of Marine Isotope Stage 5 (MIS) and represents a typical

205 interglacial endmember of Lake Ohrid's deposits. Interglacial deposits are characterized
206 by high contents of endogenic calcium carbonate (CaCO_3 , i.e. calcite), organic matter, and
207 biogenic silica (BSi, mostly diatom frustules and sponge needles), low concentrations of
208 clastic matter, **and low hematite + goethite to magnetite ratios**, respectively (Francke et
209 al., 2016; Just et al., 2016). In contrast, sample 1B-26H-cc was taken from a sediment
210 depth corresponding to MIS6, as these sediments represent the typical glacial
211 endmember at Lake Ohrid with overall low endogenic calcite, organic matter, and BSi
212 concentrations, high clastic matter contents and **high hematite + goethite to magnetite**
213 **ratios** (Francke et al., 2016; Just et al., 2016).

214 Sediment material from the Mediterranean Sea originates from piston core ESSK08-
215 CS13 (43°14.9'N 7°47.8'E), which was recovered during the 2008 ESSDIV cruise of the
216 research vessel (R.V.) *Pourquoi pas?* offshore the French alps. The core was retrieved
217 from the southwestern flank of the Var sedimentary ridge, a deep-sea turbiditic levee
218 system being mainly fed by the Var River mouth (Bonneau et al., 2014). The sediments
219 of core ESSK08-CS13 mainly consists of turbidite bed intervals intercalated with thick
220 hemipelagic sediments (Bonneau et al., 2014). Samples used for this study have been
221 taken from hemipelagic sediments corresponding to the Late Glacial Maximum (LGM,
222 MIS2, CS13-11) and to MIS 3 (CS13-14, according to the age model of Bonneau et al.,
223 2014) in order to cover the entire sedimentary variability in core ESSK08-CS13.

224 Sediment material from the Tasman Sea offshore New Zealand originates from piston
225 core TAN0513-14 (42°18'S, 169°53'E), recovered in October 2005 during the TAN0513
226 cruise of the R.V. *Tangaroa* approximately 100 km west of New Zealand's South Island
227 (Neil, 2005). The drill site is located at the northern levee of the Hokitika submarine
228 canyon system, which is the domiNat bathymetric feature in the area draining a
229 catchment area of ~1069 km². Sediment material deposited on the levees of the canyon
230 might be transported by hyper- and hypopycnal flows, and by coastal-parallel ocean
231 currents, respectively (summarized in Ryan et al., 2012). The sediments of core
232 TAN0513-14 mainly consist of siliciclastics and calcite, with CaCO_3 concentrations
233 ranging between 28 and 48 wt. % (Ryan et al., 2012). Samples T14-170 and T14-190
234 have CaCO_3 contents of 29.0 and 37.5 wt. %, and originate from MIS5.

235 **3.2 Reagents and labware**

236 The following chemicals were used within the sequential extraction experiments,
237 sample dissolution, and during column chromatography. The supplier and grade are

238 shown in brackets: 48% HF (hydrofluoric acid, Merck, Ultrapure grade), 30% HCl
239 (hydrochloric acid, Merck, Suprapure grade), 65% HNO₃ (nitric acid, Merck, Suprapure
240 grade), 31% H₂O₂ (hydrogen peroxide, Merck, Ultrapure grade), 100% CH₃COOH (acetic
241 acid, Merck, Suprapure grade), MgNO₃ (magnesium nitrate, Merck, Suprapure grade),
242 NaOAc (sodium acetate, Merck, Suprapure grade), NH₂OH • HCl (hydroxylamine
243 hydrochloride, Acros Organics, 97%), NaOH (sodium hydroxide, Merck, Emsure grade),
244 HOC(COONa)(CH₂COONa)₂ · 2H₂O (sodium citrate tribasic dehydrate, Sigma-Adrich.
245 ≥99%) . 18.2MΩ H₂O from a Milli-Q Gradient A10 filtration system was used for stock
246 solution preparation in all experiments, as well as to obtain a **near-neutral** pH of the
247 samples after each extraction experiment. To separate the solid-aqueous phases, we
248 used Eppendorf centrifuges 5804 R and 5810 at 4000 rpm for 10 minutes. Extraction
249 experiments at room temperatures were carried out using 15 ml PP (polypropylene)
250 centrifuges tubes (Tarsons Products Pvt. Ltd.) for the 'hotplate' and 'oven' experiments,
251 and 50 ml PP centrifuges tubes for the 'sonication' assisted method. Experiments
252 requiring heat (hotplate, oven, and sonication) were carried out using 50 ml PFA
253 (perfluoroalkoxy) centrifuge tubes (Savillex Corporations). We used a PL-A3 Analab
254 hotplate equipped with an A3 Analab rack to keep the 50 ml PFA centrifuge tubes in an
255 upright position and maximize heating. Sample dissolution and sample evaporation
256 after chromatography were carried out using 30 and 15 ml PFA vials (Savillex
257 Corporations), respectively.

258 **4. Experimental**

259 Samples from the Mediterranean and Tasman Sea with sand-sized material were sieved
260 to 63 μm, and further analyses were carried out on the fraction <63 μm. Sediment
261 samples from upper parts of the DEEP site core commonly comprise no sand-sized
262 material (Francke et al., 2016), and thus, the samples from Lake Ohrid were not sieved
263 to 63 μm.

264 The tested sequential extraction methods are explained in detail below. Between each
265 step, samples were rinsed two times with 18.2MΩ H₂O water, and the supernatant was
266 decanted after centrifugation at 4000 rounds per minute (rpm) for 10 minutes. After
267 rinsing, aliquots (~0.05g) of wet sediment material were taken and processed for U
268 isotope analysis in a Class 100 cleanroom at the Wollongong Isotope Geochronology
269 Laboratory (WIGL), University of Wollongong. They were first dissolved in 1 ml 48% HF

270 and 0.5 ml 65% HNO₃ at 100°C overnight, followed by 2 ml *aqua regia* at 100°C
271 overnight. Samples still showing solid residues were further treated with 31% H₂O₂ at
272 80°C overnight. Samples were then taken up in 4 ml 1.5M HNO₃ and U was separated
273 from the sample matrix using a modified chromatography method after Luo et al.
274 (1997). We used a bed of Pre-Filter resin below the TRU resin (Eichrom), in order to
275 prevent leakage of TRU resin into the elution, as organic compounds are not desirable
276 for analyses by inductively coupled plasma mass spectrometry (ICPMS). Uranium was
277 eluted in 0.1M HCL-0.3M HF. Elutions were dried down and re-dissolve in 0.3M HNO₃
278 for isotopic analysis. This was carried out on a ThermoFisher Neptune multicollector-
279 ICPMS (MC-ICPMS) at WIGL, University of Wollongong. Sample and standard solutions
280 were introduced using a PFA self-aspirating nebulizer and an ESI Apex IR desolvator. Jet
281 sample and x skimmer cones were used. Uranium-235 and ²³⁸U were collected on
282 Faraday cups, and ²³⁴U on a secondary electron multiplier (SEM) equipped with a
283 retarding potential quadrupole. Between each sample and standard, rinsing was carried
284 out with 0.3M HNO₃ – 0.1% t-Oct-C₆H₄-(OCH₂CH₂)_xOH (Triton-X) and 18.2MΩ H₂O for
285 five minutes, and instrument blanks were measured. Instrument blanks yielded
286 intensities typically <0.1% of that measured in samples and standards for any isotopes.
287 Mass bias and SEM/Faraday cup yield were quantified and used to correct isotope ratios
288 measured in samples, by analyzing synthetic standard NBL U010 (Richter and Goldberg,
289 2003) before and after each sample. Accuracy of analysis was assessed by measuring
290 NBL U005A synthetic standard (Richter and Goldberg, 2003) and was consistently
291 better than 0.18% for (²³⁴U/²³⁸U) activity ratio. Total procedure blanks were quantified
292 and contributed to less than 0.2% to the (²³⁴U/²³⁸U) activity ratio of the samples.
293 Surface area and roughness measurements were carried out by gas absorption analysis
294 on a Quantachrome Autosorb iQ. Prior to analysis, the samples were degassed for 7.5h
295 with stepwise increasing temperatures (5°C/min to 80°C, soak time 30 min, followed by
296 1°C/min to 100°C, soak time 60 min, followed by 5°C/min to 200°C, soak time 300 min).
297 Samples were then analyzed using nitrogen as the adsorbate gas. The specific surface
298 area was determined using the best fit of the Multi-point BET equation. In all
299 experiments, the correlation coefficient R² was >0.998. The fractal dimension D as a
300 measure for the surface roughness was calculated using the Neimark-Kiselev method
301 (Neimark, 1990). Due to their small size, micropores are not relevant for ²³⁴Th recoil and
302 we used the t-method by Halsey (1948) to subtract the microporous surface area from
303 the BET surface area.

304 A Phenom XL scanning electron microscope (SEM, PhenomWorld Co, The Netherlands)
305 equipped with a backscatter electron detector (BSD) and a energy dispersive X-ray
306 spectrometer (EDS) was used for elemental mapping of treated and untreated sediment
307 material on a microstructural level under high vacuum. Prior to analyses, the samples
308 were carbon coated with a Quorum Q15R E Carbon Evaporator.

309 **4.1 'Hotplate' experiments**

310 In the 'hotplate' experiments, sequential extraction was carried out following the
311 procedure described by Martin et al. (2015, Table 1), with treatment steps requiring
312 heat being carried out on a hotplate. Experiments were only conducted on sediments
313 from Lake Ohrid. Treatment steps were applied in order to remove the water soluble
314 (loosely bound elements), exchangeable (elements absorbed to mineral surfaces), acid-
315 soluble (such as carbonates), reducible (such as Fe/Mn-oxides), and the oxidisable
316 fraction (such as organic matter and sulfides). All volumes below are given for treatment
317 of 1 g of sample. Firstly, the sample was treated with 8 ml of H₂O in order to remove the
318 water-soluble fraction. Therefore, the mixture was agitated on a rotary mixer at room
319 temperature for one hour. After centrifugation, removal of the supernatant and rinsing,
320 the sample was then treated with 8 ml 1M Mg(NO₃) in order to remove the exchangeable
321 fraction. To prevent reabsorption of U to the detrital matter, 15 mg of sodium citrate
322 was added as complexing agent (Martin et al., 2015). The mixture was agitated on a
323 rotary mixer at room temperature for 50 min. After centrifugation, removal of the
324 supernatant and rinsing, the sample was then treated with 8 ml 1M NaOAc and 15 mg of
325 sodium citrate in order to remove the acid-soluble fraction. The mixture was agitated on
326 a rotary mixer at room temperature for 5 h. After centrifugation, removal of the
327 supernatant and rinsing, the sample was then treated with 20 ml of 0.04M NH₂OH-HCl in
328 25%(v/v) HOAc (pH=2) and 15 mg of sodium citrate in order to remove the reducible
329 fraction. The mixture was heated on a hotplate at 96°C for six hours. After
330 centrifugation, removal of the supernatant and rinsing, the sample was then treated for
331 removal of the oxidisable fraction in three different steps. First, it was treated with 3 ml
332 of 0.02M HNO₃, 5 ml of 31% H₂O₂, and 15 mg of sodium citrate. The mixture was heated
333 on a hotplate at 85°C for two hours. After centrifugation and removal of the supernatant,
334 the sample was then treated with 8 ml of 31% H₂O₂ and 15 mg of sodium citrate and the
335 mixture was heated on a hotplate at 85°C for three hours. Finally, after centrifugation
336 and removal of the supernatant, the sample was treated with 5 ml of 3.2/4M NH₄OAc in

337 3/4M HNO₃, and the mixture agitate on a rotary mixer at room temperature for 30
338 minutes. Following removal of the oxidisable fraction, Martin et al. (2015) applied a mild
339 HF/HCl etch, which was shown to further decrease the (²³⁴U/²³⁸U) activity ratio. This
340 decrease was attributed to a more complete removal of non-detrital matter. The lowest
341 (²³⁴U/²³⁸U) activity ratios were reported following four hours of HF/HCl etching, after
342 which dissolution of the ²³⁴U-depleted outer rim of the detrital grains (Domain 2) could
343 have resulted in the observed increase in (²³⁴U/²³⁸U) values (Martin et al., 2015). In our
344 'hotplate' experiment, we repeated the HF/HCl etch of Martin et al. (2015). For this
345 purpose, 10ml of 0.3MHF – 0.1M HCl and 15 ml of sodium citrate were added and each
346 sample was placed on a rotary mixer at room temperatures for 4 hours.

347 **4.2 'Oven' experiments**

348 The 'oven' experiments were carried out on the sediments from all three sites and follow
349 the same procedure as used in the 'hotplate' experiments. In this case, steps requiring
350 heating of the samples were carried out using an oven instead of a hotplate (Table 1). It
351 is anticipated that the use of an oven would allow to better approach the target
352 temperatures compared to the use of a hotplate (because of the small contact area
353 between the hotplate and the sample container). Thus, these experiments were
354 performed in order to test the impact of variable heating efficiency on sample treatment
355 and the (²³⁴U/²³⁸U) activity ratio and a more comprehensive removal of Domain 3
356 matter. Although the temperature of the reagent-sample mixture is likely still lower than
357 the target temperature in both experiments, we could at least ensure that the sample
358 container was at the target temperature during the 'oven' experiment. In these
359 experiments, mild HF/HCl etching was evaluated for different durations, and
360 subsamples were taken from the marine sediments after 2, 4, 6, and 8 hours (h). This
361 experiment was carried out in order to estimate the impact of applied treatment time on
362 the (²³⁴U/²³⁸U) activity ratio. In our 'oven' experiments on the sediments of Lake Ohrid,
363 sub-samples were taken after 4 hours of HF/HCl etch only.

364 **4.3 'Ultrasonication' experiments**

365 Sequential extraction using a sonication-assisted procedure follows a modified
366 description of Väisänen and Kiljunen (2005) with 1g of sediment material (Table 2). We
367 added an initial step, similar to that in the 'oven' and 'hotplate' experiments where the
368 sample was treated with 8 ml of H₂O for one hour at room temperature on a rotary

369 mixer in order to remove the water-soluble fraction. Then, the samples were treated
370 with 8 ml of 0.5M $\text{Mg}(\text{NO}_3)_2$ in order to remove the exchangeable fraction. The mixture
371 was sonicated at 20°C for three minutes (in this section, the temperature refers to that
372 of the ultrasonic bath solution). After centrifugation, removal of the supernatant and
373 rinsing, the sample was treated with 20 ml of 1M CH_3COONa at pH 5 (adjusted with
374 CH_3COOH) in order to remove the acid-soluble fraction. The mixture was sonicated at
375 20°C for 3x5 min. The mixture was agitated manually prior to and during sonication
376 every five minutes. After centrifugation, removal of the supernatant and rinsing, the
377 sample was then treated with 20ml of 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (pH=2, adjusted with
378 CH_3COOH) in order to remove the reducible fraction. The mixture was sonicated at 80°C
379 for 2x6 min. The mixture was agitated manually prior to and during sonication after 6
380 min. After centrifugation, removal of the supernatant and rinsing, the sample was then
381 treated in two steps to remove the oxidisable fraction. First, we added 26 ml of 15%
382 H_2O_2 - 0.02M HNO_3 (at pH=2). The mixture was sonicated at 20°C for 5x3 min. The
383 reaction time was increased compared to that given in Väisänen and Kiljunen (2005), as
384 samples still showed strong reactions after 3 x 3 min of ultrasonic treatment. The
385 mixture was agitated manually prior to and during sonication every 3 minutes. After
386 centrifugation, removal of the supernatant and rinsing, the sample was then treated
387 within a second step to remove the oxidisable fraction with 5 ml of 3.2 M CH_3COOH_4 in
388 20% v/v HNO_3 and the mixture was agitated manually at room temperature for one
389 minute. After centrifugation, the supernatant was removed and the sample rinsed. In
390 contrast to the 'hotplate' and 'oven' experiments, sodium citrate as complexing agent
391 was not used during the 'ultrasonication' experiments.

392 **4.4 Removal of the base-soluble fraction**

393 Biogenic silica can be abundant in lacustrine and marine sediments due to the
394 deposition of diatom frustules and/or sponge needles (Cohen, 2003). Previous studies at
395 lakes El'gygytgyn (Francke et al., 2013) and Ohrid (Francke et al., 2016; Vogel et al.,
396 2010) have shown that sodium hydroxide treatment at high temperatures have the
397 potential to remove biogenic silica from lacustrine sediments, as diatom walls dissolve
398 more rapidly at high pH conditions (Lewin, 1961). In the studies at lakes El'gygytgyn
399 and Ohrid, sediments were treated twice with 15 ml of 1M NaOH in a water bath at 85°C
400 for 30 min with continuous manual shaking. The effect of NaOH treatment on the
401 ($^{234}\text{U}/^{238}\text{U}$) activity ratio was tested on samples that underwent the sonication-assisted

402 sequential extraction on the sediments of Lake Ohrid as described in the previous
403 section. Four different treatments were tested with 20 ml of reagent, where the mixture
404 was sonicated at 80°C: 0.5M NaOH for 2x5 min, 1M NaOH for 2x5 min, 30 min or 2x30
405 min (Table 3). Prior to sample treatment, and after 5 and 30 min, respectively, the
406 samples were agitated manually.

407 5. Results and discussion

408 5.1 'Hotplate' and 'oven' experiments

409 In the 'hotplate' experiment, ($^{234}\text{U}/^{238}\text{U}$) activity ratios decrease for both Lake Ohrid
410 samples during the treatment steps targeting the exchangeable, acid-soluble, and
411 reducible fractions (Fig. 2A, Table 4). For sample 1B-26H-cc, the lowest ($^{234}\text{U}/^{238}\text{U}$)
412 value is observed after the oxidisable extraction step, while for sample 1B-17H-cc, two
413 aliquots processed separately both exhibits the lowest ($^{234}\text{U}/^{238}\text{U}$) activity ratios after
414 the reducible extraction step (Fig. 2A). **The most distinct decrease of the ($^{234}\text{U}/^{238}\text{U}$)
415 activity ratios during the 'hotplate' experiment can be observed for sample 1B-17H-cc
416 after the acid-soluble extraction step, which is probably because interglacial sediments
417 from Lake Ohrid consists of up to 90% of calcite with minor contribution from quartz
418 and other minerals (Lézine et al., 2010). Rock magnetic data from the same core as the
419 used material in this study indicate that glacial samples (such as 1B-26H-cc) are
420 characterized by a higher relative contribution of hematite+goethite against magnetite
421 than interglacial samples (such as 1B-17H-cc, Just et al., 2016). As hematite and goethite
422 are attributed to domain 3 matter, and the magnetite in the sediments of Lake Ohrid
423 mainly originates from ophiolites that crop out in the direct surroundings of the lake
424 (Just et al., 2016), a more pronounced shift towards lower ($^{234}\text{U}/^{238}\text{U}$) activity ratios
425 could be expected for sample 1B-26H-cc. Although the large scatter in the results
426 obtained from sample 1B-16H-cc hampers a detailed examination of this pattern, the
427 comparable shift in both samples from Lake Ohrid probably imply that the differences in
428 the hematite+goethite versus magnetite ratio does not significantly affect the results of
429 our extraction experiment.**

430 After 4 h HF/HCL etch, the ($^{234}\text{U}/^{238}\text{U}$) activity ratios increases for 1B-26H-cc, while it
431 does not change significantly for 1B-17H-cc. These observations suggest that the 4h
432 HF/HCl acid etch may attack the outer rind of detrital grains (Domain 2) in 1B-26H-cc,
433 while this occurs as early as during the oxidisable extraction step in sample 1B-17H-cc.

434 This pattern can be explained by the different organic matter concentrations in
435 interglacial and glacial sediments of Lake Ohrid. The total organic carbon contents (TOC)
436 is 1.3% for sample 1B-17H-cc and 0.62% for sample 1B-26H-cc (Wagner et al., 2014),
437 which can give an approximate estimate of the total organic matter concentrations in
438 the samples by multiplying TOC with 2 (e.g. Cohen, 2003). In the light of these findings,
439 the early dissolution of Domain 2 for sample 1B-17H-cc could be triggered by strong
440 oxidation reaction of organic matter. These findings imply that the 'hotplate' experiment
441 can be selective and affect samples even from the same sedimentary setting in different
442 ways. In our 'hotplate' experiments, the two aliquots processed for sample 1B-17H-cc
443 show ($^{234}\text{U}/^{238}\text{U}$) activity ratios within error for all experiments except for the reducible
444 and oxidisable fractions.

445 In the 'oven' experiment, both Lake Ohrid samples show decreasing ($^{234}\text{U}/^{238}\text{U}$) activity
446 ratios during the treatment steps targeting the exchangeable, acid-soluble, and reducible
447 fractions (Fig. 2A, Table 4), after which both samples reach minimum ($^{234}\text{U}/^{238}\text{U}$) values.
448 Both samples show higher ($^{234}\text{U}/^{238}\text{U}$) activity ratios after the oxidisable leach, although
449 this was only observed for 1B-17H-cc in the 'hotplate' experiment, explained by a
450 stronger oxidation reaction of organic matter in this sample. Since higher temperatures
451 are probably achieved during the 'oven' experiment, it is possible that the oxidation of
452 organic matter is vigorous enough to cause dissolution of Domain 2 in both samples,
453 including organic-poor sample 1B-26H-cc. Similarly to the 'hotplate' experiment, the 4 h
454 of HF/HCl etch induces no changes in ($^{234}\text{U}/^{238}\text{U}$) activity ratios for both aliquots of
455 sample 1B-17H-cc, but a higher value for sample 1B-26H-cc. This suggests no further
456 Domain 2 matter dissolution in sample 1B-17H-cc following the oxidisable extraction
457 step, whereas further dissolution takes place for sample 1B-26H-cc. In the 'oven'
458 experiment, the ($^{234}\text{U}/^{238}\text{U}$) values of the two aliquots of sample 1B-17H-cc show very
459 similar values for each step, although the reproducibility is lower as compared to the
460 'hotplate' experiment.

461 In the 'oven' experiment, samples from core ESSK08-CS13 (Mediterranean Sea) show
462 the lowest ($^{234}\text{U}/^{238}\text{U}$) values after the acid-soluble (sample CS13-11) or reducible
463 extraction steps (sample CS13-14; Fig. 2B, Table 4). While the increasing ($^{234}\text{U}/^{238}\text{U}$)
464 value following the reducible extraction step for sample CS13-11 could indicate selective
465 removal of ^{234}U from Domain 2 matter even earlier as in our 'oven' experiment on the
466 sediments from Lake Ohrid, higher activity ratios in both samples and the Lake Ohrid
467 samples strongly imply of Domain 2 matter after the oxidisable extraction step.

468 Interestingly, after reaching a maximum following the oxidisable extraction step,
469 ($^{234}\text{U}/^{238}\text{U}$) activity ratios decrease during HF/HCl etching. This is surprising as this
470 would suggest further removal of phases with a high ($^{234}\text{U}/^{238}\text{U}$) values, which is at odds
471 with the conceptual model of Fig. 1. However, activity ratios of the Mediterranean Sea
472 samples are already close to 1 after the oxidisable extraction step, which could imply
473 that Domain 2 matter has almost been completely removed from the detrital grains after
474 the oxidisable extraction step and/or at the beginning of the HF/HCl etching experiment,
475 with the remaining residue in the sample consisting of Domain 1 matter only. Further
476 mineral dissolution processes of the detrital grain during the HF/HCl etch are not
477 covered by the conceptual model of Fig. 1 and other explanations are required. During
478 emerging mineral dissolution, ^{234}U is more mobile than ^{238}U due to the preferential
479 leaching of ^{234}U from α -recoil damaged crystal lattices even in Domain 1 matter (Sheng
480 and Kuroda, 1986; Essien, 1990; Davis and Krogh, 2001; Romer and Rocholl, 2004;
481 Menozzi et al., 2016). A decrease in ($^{234}\text{U}/^{238}\text{U}$) values during etching compared to the
482 oxidisable extraction step is not observed for Lake Ohrid or Tasman Sea samples (see
483 below), which imply that dissolution of Domain 1 matter does not occur in these
484 samples. Except for the 4 h HF/HCl etch experiment, the two aliquots of sample CS13-14
485 show similar ($^{234}\text{U}/^{238}\text{U}$) values throughout the 'oven' experiments. However, values are
486 not within error of each other, similarly to the results obtained in the 'oven' experiments
487 for Lake Ohrid samples.

488 Sample T14-170 from the Tasman Sea shows decreasing ($^{234}\text{U}/^{238}\text{U}$) activity ratios
489 during the 'oven' treatment procedure, reaching a minimum value after the reducible
490 extraction step (Fig. 2C, Table 4). The ($^{234}\text{U}/^{238}\text{U}$) values then increase following the
491 oxidisable extraction and 2h HF/HCl etching steps, and remains constant for longer
492 etching durations. The highest ($^{234}\text{U}/^{238}\text{U}$) activity ratios occur after removal of the
493 exchangeable fraction. This result is also consistent with the 'sonication' experiment on
494 samples T14-170 and T14-190 (Fig. 3C) but remains surprising. The exchangeable
495 fraction is expected to be in isotopic equilibrium with the surrounding fluids during
496 mineral formation, which normally exhibit ($^{234}\text{U}/^{238}\text{U}$) activity ratios >1 . The release of
497 uranium with activity ratios between 1 and 1.05 is also unlikely to explain the higher
498 values considering the small amount of U contained in the exchangeable fraction (Plater
499 et al., 1992; Aubert et al., 2004; Virtanen et al., 2013). Consequently, a fraction with
500 ($^{234}\text{U}/^{238}\text{U}$) activity ratios significantly lower than 1 has been removed from the
501 sediment sample during the exchangeable extraction step across all experiments. In the

502 light of the conceptual model of Fig. 1, this can only be explained by Domain 2 matter
503 dissolution. An alternative explanation could be that the detrital matter was in contact
504 with waters carrying colloids characterized by low ($^{234}\text{U}/^{238}\text{U}$) activity ratios. Low
505 activity ratios of stream samples due to the presence of colloids behaving similar to bed
506 load material has for example been reported from other highly erosive settings such as
507 the rivers draining the Himalaya and the Andes (Dosseto et al., 2006a,c; Granet et al.,
508 2007).

509 Overall, these observations suggest that except for sample 1B-26H-cc during the
510 'hotplate' experiment, the oxidisable extraction step is not selective and also attack the
511 outer rim of detrital grains (Domain 2), where the ^{234}U depletion occurs. Moreover, the
512 oxidisable extraction (Lake Ohrid) and the HF/HCl etching steps (Mediterranean and
513 Tasman Sea records) can have various effects depending on the origin and composition
514 of sediments. Thus, in contrast with Martin et al. (2015), it is not clear that the HF/HCl
515 etching step should be recommended, as we even observe an increase or no change in
516 ($^{234}\text{U}/^{238}\text{U}$) activity ratios after 4 h of HF/HCl etching, using identical experimental
517 conditions ('hotplate' experiment) as in Martin et al. (2015).

518 **5.2 'Ultrasonication' experiments**

519 For the samples from Lake Ohrid, sonication-assisted sequential extraction yields
520 decreasing ($^{234}\text{U}/^{238}\text{U}$) activity ratios throughout the treatment, reaching minimum
521 values after the oxidisable extraction step (Fig. 3A, Table 4). This suggests removal of
522 non-detrital phases (Domain 3) without dissolution of the outer, ^{234}U -depleted rim of
523 the silicate grains (Domain 2). Separate treatment of two aliquots of sample 1B-17H-cc
524 yields ($^{234}\text{U}/^{238}\text{U}$) values within error of each other for almost all steps. Lower activity
525 ratios occur after the reducible extraction step using the hotplate and/or the oven
526 compared to the 'ultrasonication' experiment. This could imply that during the latter
527 experiment the removal of the reducible fraction was not complete although the results
528 show a much higher reproducibility of the sonication experiment, and thus, that the
529 'hotplate' and 'oven' treatments are more aggressive but less selective.

530 Further treatment with sodium peroxide to remove biogenic silica results in an increase
531 in ($^{234}\text{U}/^{238}\text{U}$) activity ratios, regardless of the concentration of NaOH (0.5 or 1M) or the
532 duration of the treatment (10, 30 or 60 min, Fig. 4). Biogenic silica is expected to display
533 ($^{234}\text{U}/^{238}\text{U}$) activity ratios > 1 , as a positive relationship between diatom concentrations
534 and ($^{234}\text{U}/^{238}\text{U}$) activity ratios has been observed in sediments from Lake Baikal

535 (Chebykin et al., 2004). Thus, it appears that NaOH treatment induces dissolution of the
536 ^{234}U -depleted outer rim of detrital grains (Domain 2) and optimal removal of non-
537 detrital phases is achieved after removal of the oxidisable fraction. Consequently,
538 sonication-assisted treatment using sodium hydroxide to remove biogenic silica is not
539 recommended.

540 Marine sediments from the Mediterranean and the Tasman Seas show decreasing
541 ($^{234}\text{U}/^{238}\text{U}$) activity ratio and reach minimum values after the oxidisable extraction step
542 (Fig. 3B, C, Table 4). SEM-EDS elemental mapping on sediment material of sample CS13-
543 14 yield calcium concentrations below the detection limit after ultrasonic treatment (cf.
544 Fig. 5), which can be explained by the removal of calcium carbonates (CaCO_3) from the
545 sediments. In this experiment, these samples were not treated with sodium hydroxide.
546 While ($^{234}\text{U}/^{238}\text{U}$) activity ratios increased following removal of the oxidisable fraction in
547 the 'oven' experiments, this is not observed during the sonication-assisted sequential
548 extraction. Mikutta et al. (2005) reported that treatment with H_2O_2 has the potential to
549 dissolve mineral phases such as Al- and Fe-bearing fractions, which could explain the
550 dissolution of Domain 2 during 'oven' and 'hotplate' experiments. Since (i) the
551 concentration of hydrogen peroxide used in the sonication-assisted sequential
552 extraction is half that used in the 'oven' and 'hotplate' experiments, and (ii) reaction
553 time is shorter, this could explain that it is more selective and does not attack detrital
554 grains. Although it has been shown that organic matter destruction using hydrogen
555 peroxide is usually incomplete (Mikutta et al., 2005; Plante et al., 2004; Rihs et al., 2017),
556 suggest that comparable mild treatment during the 'ultrasonication' experiments shown
557 in Table 2 yields a higher reproducibility of the analyses and thus represents a more
558 optimal method to remove non-detrital phases without affecting detrital grains.
559 However, the 'oven' experiment yields lower ($^{234}\text{U}/^{238}\text{U}$) activity ratios after the
560 reducible extraction compared to the 'sonication' method, similar to the results from
561 Lake Ohrid.

562 The two aliquots of sample CS13-14 (Mediterranean Sea) show some significant scatter
563 at each step, although they both show similar minimum values following the oxidisable
564 extraction step (Fig. 3B). Two aliquots of sample T14-170 (Tasman Sea) and 1B-17H-cc
565 (Lake Ohrid) show very similar values at most steps. These observations suggest that
566 the sonication-assisted sequential extraction presented in Table 2 can confidently yield
567 reproducible results. On the other hand, lower activity ratios after the reducible
568 extraction step are reported for the 'oven' experiments from all sites, and a significant

569 further decrease after the oxidisable extraction step can only be observed in the
570 sediments of Lake Ohrid. However, the overall low organic matter content in marine and
571 most lacustrine sediments compared to soil samples, on which most sequential
572 extraction methods have mostly been tested until today, calls for a milder chemical
573 pretreatment prior to uranium isotope analyses. Furthermore, in comparison to our
574 'oven' and 'hotplate' experiments, mild treatment within the scope of the sonication-
575 assisted extraction not only provides the best results, it is also much faster due to the
576 short reaction times. The sonication-assisted treatment is approximately five times
577 faster, which makes this method more cost-effective. Fast and cost-effective analytical
578 methods are a pre-condition for the application of U isotope analyses as a proxy for
579 erosional variability on geological time scales, since a detailed record requires
580 processing a large number of samples.

581 **5.3 Surface properties and comminution ages**

582 The impact of the 'ultrasonication' extraction method on the surface properties was
583 assessed by measuring the surface area (S) and the fractal dimension (D) on treated and
584 untreated material of samples CS13-11 and CS13-14 (Mediterranean Sea, Table 5). The
585 surface area in sample CS13-11 decreases slightly after sample treatment, whereas it
586 increases in sample CS13-14. The fractal dimension remains constant after sample
587 treatment for both samples. This implies that removed non-detrital matter has similar
588 surface properties as the detrital minerals, and that sample treatment does not
589 significantly decrease the roughness of mineral grains.

590 Assuming a recoil length for ^{234}Th of 30 nm, an initial activity ratio A_0 of 1, and a
591 sediment density of 2.65 g/cm^3 , calculated recoil fractions using equations (2) and (3)
592 vary between 3 and 20% (Table 5).

593 As explained above, it has been proposed by Bourdon et al. (2009) that a fractal
594 correction (equation (3)) should be applied to calculate the recoil fraction. This
595 correction accounts for the difference in scale of the diameter of the absorbate molecule
596 N_2 (0.354 nm) and the recoil distance of ^{234}Th (30 nm). The difference in scale results in
597 an overestimation of the recoil fraction as the measured surface area is higher as
598 relevant for ^{234}Th recoil. Applying the fractal correction in equation (3), calculated ages
599 are much older compare to ages derived from equation (2) without the fractal
600 correction. For treated samples, no numerical age can be calculated with equation (3).

601 This is because following equation (1), the activity ratio in small grains will decrease

602 over time until a new, significantly lower steady state ratio ($^{234}\text{U}/^{238}\text{U}$) = $A_0 \cdot f_4$ is
603 achieved (DePaolo et al., 2012). Using the recoil fractions of equation (3), the ($^{234}\text{U}/^{238}\text{U}$)
604 activity ratios for the samples from the Mediterranean Sea could thus only be as low as
605 0.94 for CS13-11 and 0.946 for CS13-14. These values are much higher as the measured
606 values of 0.91 for CS13-11 and 0.898 for CS13-14. This can only be solved by (a)
607 assuming the initial activity ratio A_0 in the bedrock was considerable lower than 1,
608 which is reasonable but unlikely, or (b) the recoil fractions f_4 are higher as calculated
609 with equation (3). Therefore, careful evaluation of the necessity of a fractal correction is
610 needed. Here, we argue that the fractional correction is only required if the material is
611 microporous (pores <2 nm in diameter) or mesoporous (pores between 2-50 nm in
612 diameter). Micro- and mesopores increase the measured surface area during gas
613 absorption analysis but do not contribute to the loss of ^{234}U in detrital matter as they are
614 smaller than the recoil distance of ^{234}Th (30 nm). Conversely, the surface area of non-
615 porous and macroporous (pores >50 nm in diameter) does not overestimate ^{234}Th
616 recoil, and thus, a fractal correction is not required. The shape of the adsorption-
617 desorption isotherms can be used to assess the type of material analyzed. In our case,
618 samples show Type 2 isotherms (Fig. 6), illustrating unrestricted monolayer-multilayer
619 absorption, which is characteristic for non-porous or macroporous absorbents (Sing et
620 al., 1985). This indicates that for the samples of the Mediterranean Sea, the fractal
621 correction is not required, and the recoil fraction is calculated with Equation (2).
622 Because removal of authigenic phases results in a decrease of the ($^{234}\text{U}/^{238}\text{U}$) activity
623 ratios, inferred comminution ages for treated samples are 3 to 5 times older compared
624 to untreated ones. The results obtained using equation (2) again illustrates the necessity
625 to remove any domain 3 matter from the bulk sediment composition. As the sediments
626 of samples CS13-11 and CS13-14 were deposited during MIS2 and MIS3, the inferred
627 comminution ages of 35 ± 3 ka for CS13-11 and of 25 ± 5 ka for CS13-14 are in the same
628 order as the respective depositional age of each sample. Although this can theoretically
629 be explained by extraordinary high erosion rates and analytical inaccuracies in both the
630 depositional and comminution ages, it appears unlikely given the relatively large
631 catchment area of the Var River system.

632 **6. Conclusion**

633 Sequential extraction experiments were conducted on lacustrine and marine sediments
634 from Lake Ohrid, the Mediterranean and Tasman Seas. The aim of these experiments
635 was to detect the impact of the chemical treatment steps on the ($^{234}\text{U}/^{238}\text{U}$) activity
636 ratios of the detrital matter, and determine the optimal procedure to remove non-
637 detrital phases without affecting the surface of detrital grains.

638 Experiments following the procedure from Martin et al. (2015) using different methods
639 to achieve the target reaction temperature (hotplate and oven) show that although the
640 ($^{234}\text{U}/^{238}\text{U}$) activity ratios decreases during treatment, the minimum value is achieved
641 after the reducible extraction step. The increase in ($^{234}\text{U}/^{238}\text{U}$) activity ratios after the
642 oxidisable extraction step suggests that this step is not selective and also attacks the
643 surface of detrital grains. Thus, the method presented by Martin et al. (2015) should
644 probably be modified to include a milder removal of oxidisable phases.

645 While Martin et al. (2015) recommended that oxidisable extraction step to be followed
646 by a 4 h mild HF/HCl etching, here we show that this step yields variable results
647 depending on the origin of the samples (increasing, unchanged or decreasing ($^{234}\text{U}/^{238}\text{U}$)
648 activity ratios), and thus this step is not recommended.

649 We tested the rapid sequential extraction procedure developed by Väisänen and
650 Kiljunen (2005), which utilizes sonication to reduce reaction time. Our results show that
651 ($^{234}\text{U}/^{238}\text{U}$) activity ratios decrease during treatment, reaching a minimum value
652 following the oxidisable extraction step **although after the reducible extraction step,**
653 **lower values are reported from some the 'oven' and 'hotplate' experiments.** A base-
654 soluble extraction step at the end of the procedure results in increased ($^{234}\text{U}/^{238}\text{U}$)
655 activity ratios, implying that this step attacks the surface of siliclastic grains, and is thus,
656 not recommended.

657 For the sediments of the Mediterranean Sea, gas absorption analyses yield no significant
658 modification of the surface properties (surface area and fractal dimension) after sample
659 treatment with the 'ultrasonication' method. Thus, comminution ages calculated on the
660 basis of ($^{234}\text{U}/^{238}\text{U}$) activity ratio obtained from untreated sediment material
661 considerable underestimates the catchment residence time of the detrital matter.
662 Furthermore, a fractal correction as suggested by previous studies, yields too high recoil
663 factors for the macro- and nonporous sediment material from the Mediterranean Sea,
664 resulting in a distinct overestimation of the calculated comminution ages.

665 In summary, the sonication-assisted sequential extraction presented in Table 2 allows
666 for removal of non-detrital phases without affecting the surface of detrital grains and is
667 therefore recommended as a sample treatment protocol prior to ($^{234}\text{U}/^{238}\text{U}$) activity
668 ratios analyses. This method yields reproducible results and allows processing of
669 samples up to five times faster than traditional methods. These analytical developments
670 offer a practical way to process a large number of samples for U isotope analysis. This
671 should allow the production of high-resolution records of U isotope variations in
672 sedimentary archives **with comparable sedimentary settings**. Combined to gas sorption
673 analysis, and a careful consideration of surface properties, this technique should provide
674 an improved understanding of how landscape evolution has responded to past tectonic,
675 climatic and anthropogenic disturbances.

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683 **Figures**

684 Figure 1. Conceptual model of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio behavior in response to the
685 removal of non-detrital phases (Domain 3) from lacustrine and marine sediments.
686 Optimal removal of non-detrital phases without altering the outer, ^{234}U -depleted rim of
687 a detrital grain (Domain 2) should yield the lowest ($^{234}\text{U}/^{238}\text{U}$) activity ratio. Dissolution
688 of Domain 2 would result in an increasing ($^{234}\text{U}/^{238}\text{U}$) activity ratio. After Lee (2009) and
689 Martin et al. (2015).

690
691 Figure 2. Variations in ($^{234}\text{U}/^{238}\text{U}$) activity ratios as a function of the different steps of
692 the sequential extraction protocols tested. Values correspond to the composition of the
693 solid after each indicated step. Results are shown for the 'hotplate' and 'oven'
694 experiments followed by mild HF/HCl etching undertaken on sediments from Lake

695 Ohrid (A), the Mediterranean Sea (B), and the Tasman Sea (C). Error bars correspond to
696 2σ internal standard error (smaller than the symbol size if not shown).

697

698 Figure 3. Variations in ($^{234}\text{U}/^{238}\text{U}$) activity ratios as a function of the different steps of
699 the sequential extraction protocols tested. Values correspond to the composition of the
700 solid after each indicated step. Results are shown for the sonication-assisted extraction
701 procedure, applied to sediments from Lake Ohrid (A), the Mediterranean Sea (B), and
702 the Tasman Sea (C), respectively. Error bars correspond to 2σ internal standard error
703 (smaller than the symbol size if not shown).

704

705 Figure 4. Variations in ($^{234}\text{U}/^{238}\text{U}$) activity ratios as a function of the different steps of
706 the sonication-assisted extraction procedure, followed by different extraction methods
707 to remove the base-soluble fraction. These experiments were conducted on Lake Ohrid
708 sediments only. Base-soluble – 1: 2x5 min, 80°C, 0.5M NaOH; Base-soluble – 2: 2x5 min,
709 80°C, 1M NaOH; Base-soluble – 3: 1x30 min, 80°C, 1M NaOH; Base-soluble – 3: 2x30 min,
710 80°C, 1M NaOH. Error bars correspond to 2σ internal standard error (smaller than the
711 symbol size if not shown).

712

713 Fig. 5. SEM-EDS results for untreated (A) and ‘ultrasonication’ treated (B) aliquots of
714 Mediterranean Sea sample CS13-14. Elemental mapping yields calcium (Ca)
715 concentrations below the detection limit after sample treatment, which can be explained
716 by the removal of calcium carbonates (CaCO_3) from the sample. High carbon (C)
717 concentrations in both samples are explained by carbon coating, which has been carried
718 out prior to analyses.

719

720 Figure 6. Isotherms for samples CS13-11 and CS13-14 as obtained by gas absorption
721 analysis. Upper panel: Untreated sediment material. Lower panel: The sediment
722 material was treated with the ‘ultrasonication’ extraction protocol. All samples (treated
723 and untreated) show Type II isotherms, which is indicative of unrestricted monolayer-
724 multilayer absorption as obtained from non-porous and macroporous absorbents.

725

726 **Tables**

727 Table 1. Sequential extraction method from Martin et al. (2015)

728

Target fraction	Reagent	Conditions
water soluble	8 ml H ₂ O	1 h at room temp. on rotary mixer
exchangeable	8 ml 1M Mg(NO ₃)	50 min at room temp. on rotary mixer
acid-soluble	8 mL of 1M NaOAc	5 h at room temp. on rotary mixer
reducible	20 ml of 0.04M NH ₂ OH-HCl in 25% (v/v) HOAc at pH 2	6 hr at 96°C on hotplate or in oven
oxidisable	3mL of 0.02M HNO ₃ and 5mL 31% H ₂ O ₂ at pH 2 (adjusted with HNO ₃)	2 h at 85°C on hotplate or in oven
	8ml 31% H ₂ O ₂	3 h at 85°C on hotplate or in oven
	5 mL of 3.2/4M NH ₄ OAc in 3/4M HNO ₃ ,	30 min at room temp. on rotary mixer
remaining authigenic matter?	10 ml of 0.3M HF – 0.1M HCl (mild HF/HCl etch)	2, 4, 6, or 8 h at room temp. on rotary mixer

729 Heating was achieved either by placing the samples in a graphite rack on a hotplate ('hotplate'
 730 experiments) or in a convection oven ('oven' experiments). Note variable duration for the mild HF/HCl
 731 etch.

732

733 Table 2. Sequential extraction using sonication, modified from Väisänen and Kiljunen
 734 (2005).

Target fraction	Reagent	Conditions
water soluble*	8 ml H ₂ O	1 h at room temp. on rotary mixer
exchangeable	8 ml 0.5 M Mg(NO ₃) ₂	3 min at 20°C in ultrasonic bath
acid-soluble	20 ml 1M CH ₃ COONa at pH 5, adjusted with CH ₃ COOH	3x5 min at 20°C in ultrasonic bath
reducible	20ml of 0.1M NH ₂ OH·HCl with pH at 2, adjusted with CH ₃ COOH	2x6 min 80°C in ultrasonic bath
oxidisable*	(i) 20 ml 15% H ₂ O ₂ and 6 ml 0.02 M HNO ₃ , at pH 2	5x3 min at 80°C in ultrasonic bath
	(ii) 5mL of 3.2 M CH ₃ COONH ₄ in 20% v/v HNO ₃	manually agitated for 1 min at room temperatures

735 Modified treatments, which do not follow the guideline of Väisänen and Kiljunen (2005), are marked with
 736 an asterisk.
 737

738

739 Table 3. Extraction experiments to remove the base-soluble fraction (biogenic silica)
740 using sonication.

Target fraction	Reagent	Conditions
base-soluble	20 ml 0.5M NaOH	2 x 5 min at 80°C in ultrasonic bath
base-soluble	20 ml 1M NaOH	2 x 5 min at 80°C in ultrasonic bath
base-soluble	20 ml 1M NaOH	30 min at 80°C in ultrasonic bath
base-soluble	20 ml 1M NaOH	30 min 2x30 min at 80°C in ultrasonic bath

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49 Table 4. ($^{234}\text{U}/^{238}\text{U}$) activity ratios obtained during the extraction experiments.

Site	Method	Sample	Untreated	Exchange-	acid-	Reducible	Oxidisable	base-	base-	base-	base-	etch 2h	etch 4h	etch 6h	etch 8h
			($^{234}\text{U}/^{238}\text{U}$)	ables	soluble			soluble ¹	soluble ²	soluble ³	soluble ⁴				
hotplate	1B-	1.07±	1.055±	0.94±	0.912±	0.917±	Na	Na	Na	Na	Na	Na	0.933±	Na	Na
	17H-cc	0.001	0.001	0.002	0.001	0.001							0.001		
	1B-	1.073±	1.06±	0.939±	0.898±	0.943±	Na	Na	Na	Na	Na	Na	0.932±	Na	Na
	17H-cc	0.001	0.001	0.001	0.002	0.001							0.001		
	1B-	1.013±	0.957±	0.916±	0.884±	0.858±	Na	Na	Na	Na	Na	Na	0.89±	Na	Na
	26H-cc	0.001	0.001	0.001	0.001	0.001							0.001		
oven	1B-	1.07±	1.038±	0.955±	0.899±	0.932±	Na	Na	Na	Na	Na	Na	0.942±	Na	Na
	17H-cc	0.001	0.002	0.001	0.002	0.001							0.001		
	1B-	1.073±	1.054±	0.955±	0.912±	0.94±	Na	Na	Na	Na	Na	Na	0.921±	Na	Na
	17H-cc	0.001	0.001	0.001	0.002	0.001							0.001		
	1B-	1.013±	0.968±	0.925±	0.864±	0.875±	Na	Na	Na	Na	Na	Na	0.887±	Na	Na
	26H-cc	0.001	0.002	0.001	0.001	0.001							0.001		
ultrasonication	1B-	1.07±	1.041±	0.972±	0.95±	0.917±	0.945±	0.949±	0.937±	0.942±	Na	Na	0.92±	Na	Na
	17H-cc	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.002			0.001		
	1B-	1.073±	1.048±	0.964±	0.951±	0.929±	0.946±	0.953±	0.93±	0.937±	Na	Na	0.929±	Na	Na
	17H-cc	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.003	0.003			0.001		
	1B-	1.013±	0.949±	0.93±	0.92±	0.879±	0.898±	0.899±	0.902±	0.9±	Na	Na	0.893±	Na	Na
	26H-cc	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.003			0.001		
oven	CS13-	0.977±	Na	0.928±	0.873±	0.96±	Na	Na	Na	Na	Na	0.929±	0.909±	0.92±	0.918±
	14	0.004		0.003	0.004	0.003						0.003	0.003	0.003	0.004
	CS13-	0.964±	Na	0.921±	0.872±	0.99±	Na	Na	Na	Na	Na	0.949±	0.944±	0.931±	0.932±
	14	0.003		0.003	0.004	0.004						0.002	0.004	0.003	0.003
	CS13-	0.964±	Na	0.874±	0.923±	0.973±	Na	Na	Na	Na	Na	0.948±	0.949±	0.949±	0.939±
	11	0.003		0.003	0.002	0.004						0.004	0.004	0.004	0.002
ultrasonication	CS13-	0.977±	0.958±	0.898±	0.92±	0.898±	Na	Na	Na	Na	Na	Na	Na	Na	Na
	14	0.004	0.001	0.001	0.002	0.001									
	CS13-	0.964±	0.951±	0.924±	0.906±	0.915±	Na	Na	Na	Na	Na	Na	Na	Na	Na
	14	0.003	0.001	0.002	0.001	0.002									
oven	CS13-	0.964±	0.948±	0.916±	0.913±	0.91±	Na	Na	Na	Na	Na	Na	Na	Na	Na
	11	0.003	0.001	0.001	0.001	0.001									
ultrasonication	T14-	1.047±	1.1±	0.989±	0.968±	0.977±	Na	Na	Na	Na	Na	0.99±	0.997±	0.992±	0.998±
	170	0.001	0.011	0.006	0.002	0.008						0.004	0.009	0.008	0.003
	T14-	1.047±	1.055±	0.996±	0.986±	0.989±	Na	Na	Na	Na	Na	Na	Na	Na	Na
	170	0.001	0.001	0.002	0.003	0.001									
	T14-	1.045±	1.088±	0.998±	0.994±	0.98±	Na	Na	Na	Na	Na	Na	Na	Na	Na
	170	0.001	0.002	0.001	0.001	0.002									
ultrasonication	T14-	1.059±	1.097±	0.996±	0.99±	0.992±	Na	Na	Na	Na	Na	Na	Na	Na	Na
	190	0.002	0.001	0.002	0.005	0.002									

Base-soluble¹ = 2x5 min, 0.5M NaOH; base-soluble² = 2x5 min, 1M NaOH; base-soluble³ = 30 min; 1M NaOH; base-soluble⁴ = 2x30 min, 1M NaOH

51

52 Table 5. Surface area, fractal dimension, and comminution ages for treated and ‘ultrasonication’ experiment samples CS13-11 and CS13-14.

Sample	S (m ² /g)	D	f ₄₍₂₎	f ₄₍₃₎	(²³⁴ U/ ²³⁸ U)	t, A ₀ = 1, f ₄₍₂₎ (ka)	t, A ₀ = 1, f ₄₍₃₎ (ka)
CS13-11 untreated	19.4	2.58	0.386	0.062	0.964	35±3	310±39
CS13-11 ‘ultrasonication’ experiment	18.3	2.58	0.364	0.060	0.910	100±1	Na
CS13-14 untreated	16.7	2.58	0.332	0.053	0.977	25±5	200±44
CS13-14 ‘ultrasonication’ experiment	17.2	2.58	0.341	0.054	0.898	125±1	Na

53 A₀: initial ²³⁴U/²³⁸U activity ratio. f₄₍₂₎ and f₄₍₃₎ refer to recoil fractions calculated with equations (2) and (3), respectively (see section 2). **Uncertainty of surface area analyses ±0.5**54 **m²/g**

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