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1 **Investigating the molybdenum and uranium redox proxies in a**
2 **modern shallow anoxic carbonate rich marine sediment setting of**
3 **the Malo Jezero (Mljet Lakes, Adriatic Sea)**

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14
15 **Abstract**

16 The molybdenum (Mo) and uranium (U) isotope compositions recorded in carbonate rich
17 sediments are emerging as promising paleo-redox proxies. However, the effects of early
18 diagenetic effects within the sediments on these isotope systems are not well constrained. We
19 examined the Mo and U isotopic systematics in anoxic carbonate rich sediments in a semi
20 enclosed karstic marine lake (Malo Jezero) of the Island of Mljet, Adriatic Sea.

21 Measurements of water column redox behavior in the lake since the 1950s, have shown a
22 transition from anoxic-sulfidic conditions in the deeper water column to more oxic conditions and
23 anoxia refined to the sediment and pore-waters. A 50 cm long sediment core from the deepest
24 part of the lake, show a transition from moderate to high authigenic Mo and U accumulation with
25 depth, consistent with the changing lake redox environment in the past. In the deep euxinic part
26 of the core, the authigenic Mo and U are isotopically lighter and heavier, respectively, than
27 seawater, following similar systematics as observed in other modern euxinic basins, with high,
28 but non-quantitative, Mo and U uptake into the sediments.

29 Based on Bahamas bank carbonate sediments, it has been suggested that the ²³⁸U/²³⁵U ratio is
30 ~+0.25‰ higher compared to seawater from the effects of early carbonate sediment diagenesis
31 and this carbonate vs. seawater off-set is applicable to carbonate rich sediments across the
32 geological past. The shallower part of lake sediment core was deposited under similar redox
33 conditions as the Bahamas sediments, and these sediments show an average ²³⁸U/²³⁵U ratio
34 +0.31 ± 0.01‰ (2SE) higher than seawater. Although the average ²³⁸U/²³⁵U ratios for these two
35 carbonate rich settings are similar, caution is necessary when inferring seawater ²³⁸U/²³⁵U
36 compositions from such sediments, as they contain U from different sources (e.g. diagenetic
37 uptake and carbonate-bound). The Mo isotope compositions within the same Malo Jezero
38 sediments are variable but approaches the seawater composition at low pore-water H₂S
39 concentrations. This show the potential of using the Mo isotope composition from carbonate rich

40 sediments to infer the seawater composition, however, further work is required to establish the
41 link between the Mo isotope composition and the chemistry of the pore water environment.

42 Keywords: molybdenum, uranium, redox proxies, carbonate sediments, isotopes

43

44 1. Introduction

45 Reconstructing the chemistry and redox state of the ocean in the past is critical for understanding
46 the evolution of life (e.g. [Chen et al. 2015](#); [Dahl et al. 2010](#); [Lyons et al. 2014](#)). Marine sediments
47 provide geochemical records for such reconstruction. The reliability of identifying good indicators
48 of specific environmental condition (i.e., proxies), and the processes controlling sequestration
49 from an aqueous phase into the sediments, are key points in the “reconstruction chain”. The
50 enrichment of several redox-sensitive trace elements, as well as their isotopic composition (e.g.
51 Fe, Mo, Cr, U) in (anoxic) sediments have previously shown to carry important information about
52 the redox-sensitive mechanism of seawater removal and addition to sediments at the time of
53 deposition (e.g. [Anbar and Rouxel, 2007](#); [Chen et al. 2015](#); [Dahl et al. 2010](#); [Lyons et al. 2014](#),
54 [Montoya-Pino et al. 2010](#); [Planavsky et al. 2014](#)). Yet, to fully capitalize on the potential of these
55 emerging redox-sensitive proxies for past environments, a thorough understanding of the
56 behavior in modern environments is mandatory.

57 The contrasting $^{238}\text{U}/^{235}\text{U}$ ratio (reported as $\delta^{238}\text{U}$ the $^{238}\text{U}/^{235}\text{U}$ ratio relative to the CRM 145
58 standard; [Andersen et al. 2017](#)) in different marine redox environments showed the promise of
59 $\delta^{238}\text{U}$ as a tool to investigate the history of ocean oxygenation at a global scale ([Weyer et al.](#)
60 [2008](#)). Both organic-rich sediments and carbonates have been used to reconstruct past variations
61 in oceanic $\delta^{238}\text{U}$, assuming a quantifiable relationship between the $\delta^{238}\text{U}$ in the geological archive
62 and seawater (e.g. [Brennecke et al. 2011](#); [Dahl et al. 2014](#); [Montoya-Pino et al. 2010](#)). Early
63 determination of $\delta^{238}\text{U}$ in modern and fossil carbonates suggested that these materials captured
64 $\delta^{238}\text{U}$ identical to seawater ([Stirling et al. 2007](#); [Weyer et al. 2008](#)). Further work showed, however,
65 in addition to minor isotope fractionation effects from U incorporation into some carbonates, early
66 diagenetic U addition from anoxic pore-waters may occur and increase the $\delta^{238}\text{U}$ in carbonate rich
67 sediments (e.g. [Chen et al. 2016](#); [Chen et al. 2018](#); [Romaniello et al. 2013](#); [Tissot et al. 2018](#)).
68 Consequently, correction factors of $+0.27 \pm 0.14\text{‰}$ and $+0.24 \pm 0.06\text{‰}$, respectively, were
69 suggested in order to estimate seawater $\delta^{238}\text{U}$ from bulk carbonate sediment $\delta^{238}\text{U}$ compositions
70 ([Chen et al. 2018](#); [Tissot et al. 2018](#)).

71

72 The Mo isotopic composition (reported as $\delta^{98}\text{Mo}$, the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio relative to NIST SRM =
73 $+0.25\text{‰}$; [Naegler et al. 2014](#)) of organic-rich sediments are used extensively in order to
74 investigate the history of ocean oxygenation (e.g. [Arnold et al. 2004](#); [Chen et al. 2015](#); [Dahl, et](#)
75 [al. 2010](#); [Dickson et al. 2014](#); [Goldberg et al. 2016](#); [Siebert et al. 2003](#)). Early high-precision Mo
76 isotope work showed large Mo isotope fractionations in marine Fe-Mn oxides, while near-
77 quantitative Mo removal under strongly euxinic (anoxic+sulfidic) conditions in modern Black Sea
78 yielded $\delta^{98}\text{Mo}$ near the seawater composition ($+2.3\text{‰}$) in deposited sediments. This led to the
79 framework that the oceanic $\delta^{98}\text{Mo}$ is largely controlled by the size of the oxidized seafloor and Mn
80 oxide burial, while euxinic sediment archives may record the seawater composition ([Barling et al.](#)

81 2001; Siebert et al. 2003; Nägler et al. 2011). Additional work showed lower $\delta^{98}\text{Mo}$ than seawater
82 in organic rich sediments at lower H_2S water column levels, with potential additions of Mo with
83 low $\delta^{98}\text{Mo}$ from particulate water-column shuttle processes (e.g. Arnold et al. 2004; Bura-Nakić et
84 al. 2018; Goldberg et al. 2012; Poulson et al. 2006; Noordmann et al. 2015; Poulson Brucker et
85 al. 2009; Scholz et al. 2017). This add uncertainty when $\delta^{98}\text{Mo}$ in ancient organic-rich sediments
86 is used to reconstruct ocean oxygenation in the past (Arnold et al. 2004; Barling et al. 2001; Chen
87 et al. 2015; Kendall et al. 2017; Siebert et al. 2003). It has also been suggested that non-skeletal
88 carbonates may directly record the $\delta^{98}\text{Mo}$ of the seawater (Vogelin et al. 2009; Vogelin et al. 2010,
89 Czaja et al. 2012). However, the Mo concentration in carbonates are generally low and potentially
90 influenced by early diagenetic conditions within carbonate rich sediments, emphasizing the need
91 to evaluating the processes that effect Mo and its isotopic composition during sedimentation and
92 subsequent burial (Romaniello et al. 2016).

93
94 Coupling the Mo and U isotope redox proxies may provide a better understanding of local vs.
95 global sedimentary $\delta^{238}\text{U}$ and $\delta^{98}\text{Mo}$ signatures (e.g. Andersen et al. 2018; Asael et al. 2013; Bura-
96 Nakić et al. 2018; Kendall et al. 2015; Noordmann et al. 2015). For example, organic rich
97 sediments from modern restricted euxinic basins show systematic $\delta^{238}\text{U}$ vs. $\delta^{98}\text{Mo}$ co-variation,
98 suggested to be dominantly driven by the H_2S concentration and deep-water overturning rates
99 (Andersen et al. 2018; Bura-Nakić et al. 2018). In this study the Mo and U concentrations and
100 isotope systematics were investigated in modern to near-modern carbonate rich sediments from
101 the marine lake Malo Mljet, Croatia. The deeper part of the seawater-supplied lake has shown
102 variable redox and oxic conditions in the recent past (Lojen et al. 2010; Sondi and Juračić, 2010;
103 Sondi et al. 2016) offering the potential to study U and Mo uptake under changing redox states in
104 a carbonate-dominated sediment matrix. This setting therefor serves as an important analog for
105 examining ancient carbonate sediment archives and the further understanding and utility of the
106 combined Mo and U isotope proxies.

107
108 **2. Study area**
109 The seawater-fed lakes “Malo Jezero” and “Veliko Jezero” (“small” and “big” lake) are located on
110 the western part of Mljet island, in the southern Adriatic Sea (Figure 1). The Mljet island is
111 separated from the mainland by the 8-10 km wide Mljet Canal and Veliko Jezero is connected to
112 the open sea through a shallow channel (‘Soline’ ~2.5 m depth) while another channel (~0.6 m
113 depth) connects Veliko and Malo Jezero (Lojen et al. 2010; Sondi and Juračić, 2010; Sondi et al.
114 2017). Malo and Veliko Jezero are classified as doline lakes, formed as semi-closed depressions
115 in highly permeable limestone karst of Cretaceous age (Schubert, 1909). The karstic depressions,
116 formed during the Mesozoic, have been filled with marine waters since post-glacial sea level rise
117 that intruded seawater through the karst. These submarine karstic connections are found to be
118 active today, detected from sub-bottom echo profiles (Wunsam et al. 1999). Malo Jezero has a
119 surface area of 0.25 km² with a maximal depth of approx. 30 m, while Veliko Jezero has a surface
120 area of 1.45 km² and a maximal depth of approx. 46 m (Benović et al. 2000).

121
122 Previous studies showed that anhydrous carbonate dominate the mineral composition of the Malo
123 and Veliko Jezero sediments with abundance up to ~70% within Malo Jezero (Lojen et al. 2010;
124 Sondi et al. 2017; Vuletić, 1953; Figure 2). The ratio between aragonite and calcite calcium

125 carbonate polymorphs in the sediment varies, with aragonite the most abundant comprising
126 approximately 60% of total Malo Jezero carbonates, defining the Mljet Lakes system as a site of
127 distinctive authigenic aragonite formation (Sondi and Juračić, 2010; Sondi et al. 2017).

128
129 Hydrographic data for Malo Jezero has been reported since the 1950s (e.g. Vuletić 1953; Buljan
130 and Špan 1976; Benović et al. 2001; Cuculić et al. 2008; Sondi and Jurčić 2010; Vilibić et al.
131 2010). The pH of the Malo Jezero waters varies between the yearly seasons with lowest pH values
132 during winter (e.g. 8.02 ± 0.01 at the surface in January 2008), and highest pH values during
133 summer (e.g. 8.30 ± 0.01 at the surface in July 2005). In the early 1950s the salinity in Malo
134 Jezero bottom waters was in the range of 36-38 while surface waters were characterized by lower
135 salinity ~ 29 (Buljan and Špan, 1976). An increase in salinity was noticed in the 1990s with the
136 Malo Jezero bottom waters surpassing salinity of 38.5 (Benović et al. 2000). Spatial and temporal
137 variations of water temperature in the Malo Jezero show typical seasonal variability, reflecting the
138 air temperature changes, with the surface Malo Jezero waters being colder during the winter and
139 warmer during the summer, compared to Adriatic open sea waters. A thermocline appears in early
140 summer, deepening towards early autumn before vanishing during the winter. Records from 1997
141 to 1999 showed that in the summer months the thermal stratification occurred in the layers
142 between 10-15 m (Malo Jezero) and 15-20 m (Veliko Jezero). During the periods of thermal
143 stratification, the bottom water layers were low in oxygen, with oxygen saturation reaching
144 minimum of 4% (Malo Jezero) and 17% (Veliko Jezero) in October 1997 (Benović et al. 2000).

145
146 Anoxic and euxinic conditions in the water column of Malo and Veliko Jezero has not been
147 observed within the last couple of decades (Jasprica et al. 1995; Benovic et al. 2000). However,
148 vertical sediment profiles of redox sensitive elements within Malo Jezero, indicate the occurrence
149 of euxinic conditions in the bottom water layer of Malo Jezero and a rapid disappearance of such
150 conditions later in the lake history (Sondi et al. 2017). Reported $[H_2S]$ (Buljan and Špan, 1976) at
151 25 m water depth for the 1951 to 1961 period were in the range from 6 to $155 \mu\text{mol l}^{-1}$, showing
152 seasonal variations with the highest $[H_2S]$ during the winter-autumn period (Supplementary
153 Information Table 1). Also, the lake $[H_2S]$ data shows that the extent of anoxia was variable, with
154 the chemocline rising upwards during the winter-autumn period. The variable extent of anoxia is
155 likely linked to the degree of Malo Jezero water mass exchange with Veliko Jezero and the open
156 sea during the year. Sudden environmental change took place in the early 1960s, as a
157 consequence of the enlargement and deepening of the Soline Channel at that time. This resulted
158 in significantly increased water exchange between the open ocean and the lakes with the
159 disappearance of euxinic conditions in Malo Jezero and occurrence of oxic conditions in the
160 bottom waters as determined in July 1961 (Buljan and Špan, 1976). The irregular occurrence of
161 dark layers of different thickness in the laminated sediments deposited before 1960s, indicates
162 that euxinic conditions in Malo Jezero were not permanent, but were interrupted with shorter or
163 longer oxic to suboxic periods (Supplementary Information Table 1 - Buljan and Špan, 1976;
164 Sondi et al. 2017).

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3. Sampling

Undisturbed sediment cores up to 50 cm long were collected in Malo Jezero using an Uwitec gravity corer in the period 2007-2010 at depths of 30 meter (core C1), 22 meter (core C2) and 13 meter (core C3). In order to extract pore water from sediments, sediment cores were sectioned into 2 cm segments in a glove box under an inert nitrogen atmosphere immediately after sampling. The sampled segments were centrifuged at 4000 x g for 30 minutes and the pore water was extracted using a plastic syringe and filtered through 0.45 µm Minisart cellulose acetate (Sartorius) filters under an inert nitrogen atmosphere. The segments were then freeze-dried and stored until further geochemical analyses were performed. Samples of the surrounding rocks, Cretaceous limestone and Jurassic dolomite, and the two main types of soil samples, *terra rossa* and dark humus rich soil, were also collected. Lake water was collected using a Niskin sampler system at three different depths (0, 12 and 25 m) and stored in acid cleaned plastic bottles.

4. Methods

4.1. Sample preparation

All chemical preparation and sample analyses were performed in the isotope facilities at the Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Switzerland, unless stated otherwise.

Water sample aliquots (~20 ml) were taken for isotope analyses, aiming for a total of 20–50 ng U and 150–250 ng Mo. Aliquots were transferred into pre-cleaned Teflon beakers, and spiked with the IRMM–3636 ^{236}U – ^{233}U double-spike (Richter et al. 2008) aiming for a 1:35 spike to sample ratio, and a ^{100}Mo – ^{97}Mo double-spike (approach adapted from Siebert et al. 2001) aiming for a 1:1 spike to sample ratio. These were subsequently dried down (at ~100 °C) and prepared for isotope analyses following methods described in Bura-Nakić et al. (2018). Briefly, following the seawater drying step, a large NaCl precipitate forms. This precipitate is leached using 10 ml 7 N HCl for 24 hours, a treatment which dissolves Mo, U and other metals but minimises dissolution of NaCl. After centrifugation (3500 x g for 10 minutes) the supernatant was removed, dried down and re-dissolved in 5 ml 7N HCl in preparation for column chromatography. The recoveries of both U and Mo in the supernatant were consistently >90% using this procedure (Bura-Nakić et al. 2018).

Approximately 50–100 mg of the sediment and soil samples were dissolved for analyses. Full dissolution of samples were carried out using standard protocols for silicates, involving mixtures of HF–HNO₃–HCl and H₂O₂ in the same manner as described in Andersen et al. (2013). After drying, the samples were dissolved in 10 ml 6 N HCl. One small aliquot was taken to determine elemental concentrations while another aliquot, containing 20–50 ng U and 150–250 ng Mo, was added to pre-cleaned Teflon beakers, spiked with the U and Mo double-spikes, and left to equilibrate on a hotplate before being dried down (at ~100 °C). Samples were then re-dissolved in 5 ml 7 N HCl in preparation for column chromatography.

212 4.2. Column chromatography

213 A one step purification and U–Mo separation procedure was conducted using RE Resin (Triskem
214 technologies) in custom-made shrink-fit Teflon columns (~0.2 ml resin reservoir) following the
215 procedure of Bura-Nakić et al. (2018). The resin was added to the Teflon columns and pre-
216 cleaned using 2 ml 0.1 N HCl–0.3 N HF, rinsed with MQ water, and pre-conditioned with 2 ml 7
217 N HCl. After the samples were loaded in 5 ml 7 N HCl, the matrix was eluted with 10 ml 1 N HCl.
218 The Mo and U fraction were eluted from the resin and collected separately, first with 5 ml 0.2 N
219 HCl, followed by 5 ml 0.1 N HCl–0.3 N HF, respectively. The column chromatography procedure
220 yielded high purity Mo and U fractions with low Mo and U blanks (<13 pg and <22 pg for Mo and
221 U, respectively; Bura-Nakić et al. 2018). Prior to mass spectrometry, the U fractions were dried
222 down and fluxed on a hotplate for 24 hours in a 1 ml 1:1 mixture of concentrated HNO₃ and H₂O₂,
223 while the Mo fractions were merely dried down. The purified Mo and U were then re-dissolved in
224 1 ml 0.3 N HNO₃ and 1 ml 0.2 N HCl, respectively, for mass spectrometry. The column separation
225 and purification procedure was tested by processing two open Atlantic Ocean samples, with
226 measured Mo and U isotopic compositions in good agreement with previously reported values.

227

228 4.3. Elemental concentration measurements

229 The concentrations of selected elements (see Supplementary Information Tables 2 and 3) were
230 measured in 0.3 N HNO₃ using a Thermo–Finnigan Element XR ICP–MS in both low and medium
231 resolution mode, following measurement protocols in Andersen et al. (2013, 2016). A primary in-
232 house concentration standard was interspersed with three unknowns and a secondary standard
233 (BCR–2) was used to monitor the accuracy and reproducibility of the method. Repeated
234 measurements of BCR–2 gave reproducibilities better than ± 10% (1 S.D.) and mean values within
235 ± 10% of certified concentrations (see Andersen et al. 2016).

236

237 4.4. Molybdenum and uranium isotope measurements

238 Isotope ratios were measured on a Neptune (Thermo–Finnigan) MC–ICPMS equipped with an
239 AridusII, auto-sampler (CETAC) using a PFA nebulizer and spray chamber (CPI) sample
240 introduction system. Instrumental set-up details are given in Archer and Vance (2008) for Mo
241 isotopes and Andersen et al. (2016) for U isotopes. Analysis of spiked in-house CPI standard
242 (standard/spike ratios in the range of 0.1 to 5) as well as the open-ocean seawater were used to
243 test the reproducibility and accuracy of the Mo isotope method. The long-term average and ±2
244 S.D. reproducibility during the period of this study, gave $\delta^{98}\text{Mo} = -0.02 \pm 0.04\text{‰}$ relative to NIST
245 SRM = +0.25‰ (Bura-Nakić et al. 2018). Analysed seawater samples gave $\delta^{98}\text{Mo}$ of $+2.37 \pm$
246 0.03‰ , in agreement with previous data for seawater $\delta^{98}\text{Mo}$ (e.g. Nakagawa et al. 2012). In
247 addition to $^{238}\text{U}/^{235}\text{U}$, $^{234}\text{U}/^{238}\text{U}$ ratios were measured and reported as ($^{234}\text{U}/^{238}\text{U}$) activity ratios
248 (using half-lives of Cheng et al. 2013). The verification of the U double spike method was carried
249 out via repeated measurement of the in-house CZ–1 uraninite standard and open-ocean seawater
250 samples. The long-term average and ±2 S.D. reproducibility for the CZ–1 standard were $-0.04 \pm$
251 0.07‰ for $\delta^{238}\text{U}$ and 0.9996 ± 0.0025 for ($^{234}\text{U}/^{238}\text{U}$) (Bura-Nakić et al. 2018), in agreement with
252 previously reported values (Andersen et al. 2016; Stirling et al. 2007). Uranium isotopic analysis
253 of five seawater samples gave a $\delta^{238}\text{U} = -0.39 \pm 0.04\text{‰}$ and ($^{234}\text{U}/^{238}\text{U}$)_{act} = 1.147 ± 0.003 (Bura-
254 Nakić et al. 2018), again in very good agreement with reported data for seawater (Andersen et al.

255 2010, 2014; Tissot and Dauphas, 2015; Weyer et al. 2008). See Bura-Nakić et al. 2018 and
256 Andersen et al. (2016) for further details on methods and performance.

257

258 4.5. Other analyses

259 The total carbonate content was determined volumetrically with a Scheibler's apparatus (Allison
260 and Moodie, 1965) at the Ruđer Bošković Institute in Zagreb, Croatia. Sulfide concentrations were
261 analysed by linear sweep voltammetry (LSV) within 8 hours of sampling according to established
262 procedures (Bura-Nakić et al. 2009; Ciglencčki et al. 2005; Ciglencčki et al. 2015) at the Ruđer
263 Bošković Institute marine station situated near Šibenik. Electrochemical measurements were
264 performed with μ Autolab Electrochemical Instruments (EcoChemie) connected with 663VA Stand
265 Metrohm electrode.

266

267 5. Results

268

269 5.1. Elemental concentrations

270

271 5.1.1. Sediments and pore-waters

272

273 The mineral composition of sediment cores taken from the lake sediments of the Malo Jezero at
274 cores C1, C2 and C3 (Figure 1) showed a high carbonate content, dominated by authigenic
275 aragonite (comprising ca. 70-90% of the carbonate content) with minor calcite, magnesium calcite
276 and dolomite. The calcite and dolomite originated from surrounding source rocks of Jurassic-
277 Cretaceous limestones and dolomites. Besides the carbonate phases the sediments also
278 contained small amount of mica, quartz, kaolinite and framboidal pyrite. The total carbonate
279 content within the investigated sediments is high, comprising up to ~70% in cores C1 and C2 and
280 reaching up to ~90% in core C3. The $[\text{Sr}]_{\text{bulk}}$ is also relatively high, ranging from 3078 to 4158 μg
281 g^{-1} . Concentrations of sedimentary organic carbon in core C1 were measured in Lojen et al.
282 (2010) with C_{org} (wt%) varying between 1.4 to 2.1%, with the lowest C_{org} at 13 cm depth. Using
283 marine and terrestrial $\delta^{13}\text{C}$ endmembers signatures, Lojen et al. (2010) estimated the fraction of
284 terrestrial organic C ranging from 53 to 76%.

285

286 The distributions of typical lithogenic elements (e.g. Al, Ti and Li) display similar behavior with
287 sediment depth. The concentrations of Al (0.38 to 6.4%), Ti (0.03 to 0.20%) and Li (0.31 to 0.46%)
288 are generally low, but show a gradual increase with depth in each core, while the two deepest
289 cores (C1 and C2) have higher lithogenic element concentrations than the shallower core C3
290 (Figure 2 and Supplementary Information Table 2).

291

292 The bulk concentrations of the investigated redox sensitive elements ($[\text{Mo}]_{\text{bulk}}$, $[\text{U}]_{\text{bulk}}$ and $[\text{V}]_{\text{bulk}}$)
293 display somewhat contrasting behavior. The behavior of $[\text{V}]_{\text{bulk}}$ is similar to that of the lithogenic
294 elements, with lower $[\text{V}]_{\text{bulk}}$ in core C3 compared to cores C1 and C2. Similarly, a moderate
295 increase in $[\text{U}]_{\text{bulk}}$ (from 2.2 to 8.4 $\mu\text{g g}^{-1}$) can be observed in all three cores, this $[\text{U}]_{\text{bulk}}$ increase
296 is intensified below the ~20 cm sediment horizon for the two deepest cores. These sediment
297 horizons also have high $[\text{Mo}]_{\text{bulk}}$ (25 to 78 $\mu\text{g g}^{-1}$), with a sharp contrast to lower $[\text{Mo}]_{\text{bulk}}$ (2.1 to 20

298 $\mu\text{g g}^{-1}$) above the ~20 cm sediment horizon in core C1 (Figure 2 and Supplementary Information
299 Table 2).

300
301 Pore-water $[\text{H}_2\text{S}]$ for core C1 were determined as part of the present study and combined with
302 already published pore-water data on $[\text{Mo}]$, $[\text{U}]$, $[\text{Fe}]$ and $[\text{Mn}]$ (Sondi et al. 2017; Supplementary
303 Information Table 4). The $[\text{H}_2\text{S}]$ increase with increasing core depth (0 to 755 $\mu\text{mol l}^{-1}$) with a
304 sharp increase between the 11 to 17 cm sediment horizons, which likely correspond to the zone
305 where reactive Fe diminishes and reduced Fe is predominating in the form of pyrite (Sondi et al.
306 2017). The pore-water concentration of dissolved Fe and Mn are highest in the subsurface
307 sediment layer at 1 cm depth, reflecting the position of the oxic-anoxic boundary. The pore-water
308 $[\text{Mo}]$ in the top sediment layer (107 nmol l^{-1}) closely match overlying bottom water $[\text{Mo}]$ (~110
309 nmol l^{-1}), while it generally decreases and remains lower through the core (~50-90 nmol l^{-1})
310 indicating removal of Mo from the pore-waters. The $[\text{U}]$ in the pore-waters is exhibiting significant
311 decrease (more than 50% within the subsurface layer) in comparison to the $[\text{U}]$ in the overlying
312 bottom waters, implying substantial U removal from the pore-waters.

313
314 **5.1.2 Catchment area and lake water**
315 Major and trace element concentrations were determined in the soil (*terra rossa* and humus) as
316 well as karst host rock samples (limestone or dolomite) collected close to the lake (Supplementary
317 Information Table 3). The carbonate host rock samples are characterised by low $[\text{Sr}]$ (92 to 392
318 $\mu\text{g g}^{-1}$) as well as low $[\text{Al}]$ (153 to 970 $\mu\text{g g}^{-1}$), $[\text{Li}]$ (0.24 to 1.4 $\mu\text{g g}^{-1}$) and $[\text{Ti}]$ (7 to 49 $\mu\text{g g}^{-1}$). The
319 $[\text{Mo}]$ within the host rock samples is low (0.14 to 0.73 $\mu\text{g g}^{-1}$), similarly to what is typically observed
320 for carbonates (Vogelin et al. 2009) while the $[\text{U}]$ and $[\text{V}]$ are higher (1.3 to 3.6 and 3.5 to 23 μg
321 g^{-1} , respectively). Soil samples are characterised by $[\text{Al}]$, $[\text{Ti}]$ and $[\text{Li}]$ approximately three orders
322 of magnitude higher than the host rock samples. Compared to the host rock samples, the soil
323 samples have similar $[\text{Sr}]$ (61 to 102 $\mu\text{g/g}^{-1}$) while $[\text{Mo}]$ (1.4 to 4.0 $\mu\text{g g}^{-1}$), $[\text{U}]$ (2.4 to 4.0 $\mu\text{g g}^{-1}$)
324 and $[\text{V}]$ (72 to 168 $\mu\text{g g}^{-1}$) are all higher.

325
326 The $[\text{Mo}]$ and $[\text{U}]$ were measured in filtered waters sampled at 0, 12 and 25 m depth. These show
327 a narrow concentration range from 103.3 to 110.2 nmol l^{-1} and 13.0 to 13.8 nmol l^{-1} for $[\text{Mo}]$ and
328 $[\text{U}]$, respectively, close to average open ocean compositions (Supplementary Information Table
329 5).

330
331 **5.2 Mo and U isotopic composition**

332
333 **5.2.1. Sediments**
334 The bulk sedimentary Mo isotope compositions ($\delta^{98}\text{Mo}_{\text{bulk}}$) generally increase with depth within
335 the three sediment cores (Figure 2 and Table 1). The $\delta^{98}\text{Mo}_{\text{bulk}}$ compositions in core C1 varies
336 between +1.8 to +1.4‰, apart from the top sample at 1 cm depth with a lower $\delta^{98}\text{Mo}_{\text{bulk}}$ (+1.0‰).
337 Core C2 is characterized by $\delta^{98}\text{Mo}_{\text{bulk}}$ in the range from +2.4 to +1.7‰ while core C3 shows
338 variable Mo isotope compositions, including the lowest, $\delta^{98}\text{Mo}_{\text{bulk}}$ (+1.6 to +0.7‰).

339
340 The cores exhibit limited variation in the bulk sedimentary $\delta^{238}\text{U}$ compositions ($\delta^{238}\text{U}_{\text{bulk}}$), ranging
341 from +0.03 to -0.29‰. Core C1 show the least variable $\delta^{238}\text{U}_{\text{bulk}}$ (-0.05 to -0.15‰), followed by
342 core C2 (+0.02 to -0.13‰), while core C3 have $\delta^{238}\text{U}_{\text{bulk}}$ of -0.29‰ for the top 1 cm and +0.03‰

343 at 23 cm depth. The $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ for the bulk sediments increase with depth in all three cores
344 (Figure 2 and Table 1). Cores C2 and C1 have the highest $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ (1.065 to 1.033) while
345 core C3 show lower $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ (from 1.023 to 1.000 for the 1 cm depth sample).

346

347 **5.2.2. Soil and water samples**

348 The measured $\delta^{98}\text{Mo}$ (average $+2.41\pm 0.02\text{‰}$), and $\delta^{238}\text{U}$ (average $-0.36\pm 0.02\text{‰}$) in the Malo
349 Jezero lake waters at 0, 12 and 25 m depth (Supplementary Information Table 5) are close to the
350 open ocean ($\delta^{98}\text{Mo}_{\text{SW}}=+2.37\text{‰}$ and $\delta^{238}\text{U}_{\text{SW}}=-0.39\text{‰}$; Andersen et al. 2014; Nakagawa et al. 2012).
351 The $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ for the same lake water samples (1.136 to 1.138) are slightly lower than the
352 open ocean seawater (1.147; Andersen et al. 2010). The *terra rossa* and the humus soil samples
353 were characterized by variable $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ (1.102 and 0.977), but similar $\delta^{238}\text{U}$ (-0.28‰ and -
354 0.22‰) and $\delta^{98}\text{Mo}$ ($+0.53\text{‰}$ and $+0.62\text{‰}$), see Table 1.

355

356 **6. Discussion**

357

358 The main aim is to broaden our understanding of $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ signatures within carbonate
359 rich sediments under changing redox conditions. The discussion on the sedimentary $\delta^{98}\text{Mo}$ and
360 $\delta^{238}\text{U}$ budget therefor primarily focusses on the deep Malo Jezero sediments (core C1), due to
361 the available literature data (Sondi et al. 2017) and the most complete $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ data-set.

362

363 **6.1. The sources of Mo and U in the sediments of Malo Jezero**

364 The uptake of the redox-sensitive U, Mo and V in the Malo Jezero sediments will be impacted by
365 various biogeochemical and physical processes. Three main sources may be considered
366 important for the sediments in this particular system; (1) the addition from detrital material, e.g.
367 siliciclastic and carbonate, (2) the formation of authigenic carbonate phases in the lake and (3)
368 other transport uptake mechanisms, either from authigenic processes directly within the waters
369 and/or pore-water. Below, these three potential sources are discussed in turn.

370

371 (1) Sondi et al. (2017) concluded that soils were an important source of material deposited in the
372 Veliko and Malo Jezero based on the similar geochemistry of soil and sediment from sampled
373 cores. However, the soils surrounding the lake are heterogenous and in order to estimate the
374 possible influence of this detrital material on the sediment geochemistry, two general detrital end-
375 members can be defined; limestone/dolomite vs. siliciclastic (clay) dominated soils (Figure 3).
376 These two end-members have distinct geochemical signatures. The Malo Jezero sediments
377 shows a near-linear relationship between typical lithogenic elements (e.g. [Al] vs. [Ti] and [Al] vs.
378 [Li]), suggesting that the Malo Jezero lithogenic fraction in the sediments are a physical mixture
379 of the two generalised detrital end-members (Figure 3). Vanadium concentrations in the
380 sediments also show similar mixing relationship with [Al], while both [U] and [Mo] show generally
381 higher concentrations than can be explained by simple mixing of these two end-member sources
382 (Figure 3). This suggests that, while the redox sensitive V are likely dominated by the detrital
383 fraction, additional source(s) of Mo and U uptake is/are required to explain the sediment data.

384

385 (2) The mineralogy of the sediments within Malo Jezero revealed that aragonite is the dominating
386 carbonate fraction. This source of authigenic-formed aragonite in the lake is manifested in high

387 sediment [Sr] (3000-5000 $\mu\text{g g}^{-1}$) compared to the soil and limestone host rocks (61 to 392 $\mu\text{g g}^{-1}$) a feature also observed in previous studies (Sondi and Juračić, 2010; Sondi et al. 2017). The
388
389 authigenic-formed aragonite could provide an additional source of U and Mo to the sediments.
390 However, marine aragonite is typically characterized by low [Mo] (Voegelin et al. 2009;
391 Romaniello et al. 2016) and no correlation is observed between [Mo] and [Sr] (Figure 3),
392 suggesting limited Mo addition from this source. While [U] is normally relatively high in marine
393 aragonite (2-4 $\mu\text{g g}^{-1}$ range; Dunk et al. 2002), there is no obvious correlation between [U] and
394 [Sr] (Figure 3), suggesting that the U incorporation into this lake aragonite phase is minor. This
395 suggests that the relatively high [Mo] and [U] observed in the deeper parts of cores C2 and C1
396 must be dominated by other uptake mechanism(s).

397
398 (3) Authigenic uptake of Mo and U in sediments often occur under reducing conditions. For both
399 U and Mo, early *in-situ* diagenetic precipitation is observed in a range of environments with euxinic
400 pore-waters (e.g. Chen et al. 2018; McManus et al. 2006; Morford et al. 2005; Romaniello et al.
401 2013, 2016; Zheng et al. 2002). High Mo accumulation also occur in strongly euxinic waters,
402 presumably via the formation of sulfidic molybdate species followed by particulate organic
403 scavenging or formation and scavenging of authigenic FeMoS_4 minerals (e.g. Algeo and Lyons,
404 2006; Erickson and Helz, 2000; Helz et al. 1996; Helz et al. 2011; Helz and Vorlicek, 2019). Other
405 potential important sources of addition of Mo and U in anoxic sediments may be associated
406 directly with deposited organic matter (e.g. Kowalski et al. 2013; King et al. 2018; Zheng et al.
407 2002) and (particularly for Mo) Fe-Mn shuttle processes (e.g. Algeo & Lyons 2006; Scholz et al.
408 2017). All three cores show an increase in [U] with depth (Figure 2) suggesting increasing U
409 addition to the sediments with decreasing redox potential at depth in the pore waters. The highest
410 [U] ($>5 \mu\text{g g}^{-1}$) is observed at depths below 20 cm in cores C1 and C2, similar to the zones of the
411 highest [Mo] ($>40 \mu\text{g g}^{-1}$). In contrast, the [Mo] is much lower in the horizons above ($<5 \mu\text{g g}^{-1}$)
412 and there is little evidence for any Mo addition in core C3 (Figure 2).

413
414 **6.2. Quantification of the authigenic U and Mo fractions in the Malo Jezero sediments**
415 With a general separation of the different sources of U and Mo in the sediments, it is possible to
416 further quantify the authigenic U and Mo fractions, and associated isotope signatures, to provide
417 better constraints on the processes governing the mechanisms of U and Mo enrichment.

418
419 The daughter ^{234}U to parent ^{238}U activity ratio, $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ can provide an effective method to
420 distinguish between U from an authigenic or detrital source in Holocene-aged sediments (e.g.
421 Holmden et al. 2015; Andersen et al. 2016). This stem from modern seawater $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ is
422 $\sim 15\%$ enriched in ^{234}U due to α -recoil processes, while older detrital lithogenic material is normally
423 characterized with a $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ near secular equilibrium (Andersen et al. 2010). The
424 $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ in the surface sample of core C3 is in secular equilibrium, implying negligible
425 authigenic U and can therefore be considered a detrital end-member. This sample is
426 characterized by $[\text{U}]_{\text{bulk}}$ of $2.2 \mu\text{g g}^{-1}$, U/Al ratio of $5.8 \times 10^{-4} \text{ g/g}$ and $\delta^{238}\text{U}$ of -0.29‰ . This
427 sediment sample is also characterized by high CaCO_3 and [Sr] suggesting that, as already
428 discussed, the contribution of U from authigenic aragonite has a minor impact on the sedimentary
429 U budget. Sediments with higher [U] show increasing $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ consistent with increasing
430 authigenic U accumulation. The sediments show a broadly linear correlation between $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$

431 vs. $1/[U]$, suggesting a mixture between detrital and authigenic U (Figure 4). However, the inferred
432 authigenic end-member of this linear mixing line has a $(^{234}U/^{238}U)_{act}$ of ~ 1.09 , a value significantly
433 lower than the measured $(^{234}U/^{238}U)_{act}$ in the lake waters (~ 1.14). The origin of this relatively low
434 authigenic $(^{234}U/^{238}U)_{act}$ estimation is not clear. One possibility is incongruent calcite dissolution,
435 as suggested to occur within the reducing Malo Jezero sediments (Lojen et al. 2010), releasing
436 U with low $(^{234}U/^{238}U)_{act}$ which then mixes with seawater-derived U in the pore-waters. Alternative
437 suggestions may be related to additional groundwater input or dissolution of karst during seawater
438 flow-through in the cave systems, both adding U with low $(^{234}U/^{238}U)_{act}$. Lower than seawater
439 $(^{234}U/^{238}U)_{act}$ was also observed in the seawater lake Rogoznica, Croatia, which is also fed through
440 karst cave systems (Bura-Nakić et al. 2018). Whichever the mechanism, the uncertainties in the
441 $(^{234}U/^{238}U)_{act}$ for the both the detrital and authigenic U end-members, limits the usage of
442 $(^{234}U/^{238}U)_{act}$ to quantify the authigenic U contribution in the Mjet lake sediments (see also section
443 6.4).

444
445 Instead, the authigenic to detrital components for both U and Mo can be estimated comparing
446 these to Al, typically used for estimating authigenic enrichment factors (EF; e.g. Tribouillard and
447 Algeo, 2009). However, the detrital fraction of U and Mo in each sediment horizon is a mixture
448 between the (i) limestone/dolomite and (ii) their weathering products in the form of *terra rossa* and
449 organic rich soils (as shown by the Al vs. Ti correlation, Figure 3). Thus, using only one average
450 $[U]/[Al]$ or $[Mo]/[Al]$ ratio for the detrital fraction would lead to under- and/or overestimation of the
451 authigenic U and Mo component. Instead, to estimate the U and Mo detrital vs. authigenic
452 contribution, a linear regression line can be estimated between the two generalized detrital end-
453 members in the $[U]$ or $[Mo]$ vs. $[Al]$ space, which reflect the degree of weathering of the detrital
454 source (Figure 5). Using this approach, the $[U]_{auth}$ and $[Mo]_{auth}$ fractions are estimated to range
455 between 14 to 68%, and 4 to 98% of the bulk, respectively (Table 2). Both $[Mo]_{auth}$ and $[U]_{auth}$ show
456 progressive increases with depth in all the cores. Furthermore, both cores C2 and C1 show a
457 large increase in $[Mo]_{auth}$ between 18 to 25 cm depth, while C3 core show much lower overall
458 $[Mo]_{auth}$ (Figure 6). The two upper part of core C3 (1 and 9 cm depth) are characterized by very
459 low $[Mo]_{bulk}$ (0.18 and $0.13 \mu g g^{-1}$, respectively) close to the average carbonate catchment $[Mo]$
460 ($0.29 \mu g g^{-1}$, $n=5$), showing the $[Mo]_{auth}$ is negligible if at all present in these sediments. The
461 estimated $[U]_{auth}$ for the top 1 cm in core C1 is the lowest within the investigated sediments (0.33
462 $\mu g g^{-1}$), in agreement with the minimal authigenic U uptake based on the $(^{234}U/^{238}U)_{act}$ composition.

463 464 **6.3. Estimating the authigenic U and Mo isotope signatures in the Malo Jezero sediments**

465 The estimation of $\delta^{238}U_{auth}$ and $\delta^{98}Mo_{auth}$ build on $[U]_{auth}$ and $[Mo]_{auth}$ calculations (Figure 6).
466 Combining the relative size of the detrital component with an estimated isotopic composition can
467 provide an estimated isotope composition of the authigenic fraction. As the detrital fraction for
468 each sediment sample is a mixture between the two detrital end-members, the isotope
469 composition also needs to be estimated for each sediment sample. For U, both end-member have
470 very similar $\delta^{238}U$ (the clay fraction of -0.28‰ and carbonate/dolomite fraction of -0.29‰ , based
471 on the 1 cm sediment sample in core C3) and both are similar to average 'bulk Earth' and
472 continental crust $\delta^{238}U$ estimates (Andersen et al. 2017; Tissot et al. 2015). For the detrital Mo,
473 the $\delta^{98}Mo$ of the clay fraction were estimated to be $+0.58\text{‰}$ (average of the measured soils) while
474 the carbonate/dolomite fraction were estimated to be $+1.03\text{‰}$ (based on the 1 cm sediment

475 sample in core C3), both slightly higher than typically used for detrital $\delta^{98}\text{Mo}$ compositions (~ 0.0
476 to $+0.3\text{‰}$; Kendall et al. 2017). The $\delta^{238}\text{U}_{\text{auth}}$ and $\delta^{98}\text{Mo}_{\text{auth}}$ estimates (Figures 6 and 7 and Table
477 2), have uncertainties estimated based on propagated measurement errors scaled to the relative
478 size of the detrital component (see Andersen et al. 2014 for details). This error propagation leads
479 to increasing uncertainty estimates with increasing detrital contribution. Therefore, detrital-
480 dominated sediments with uncertainties $>0.4\text{‰}$ ($\pm 2\sigma$) on the $\delta^{238}\text{U}_{\text{auth}}$ or $\delta^{98}\text{Mo}_{\text{auth}}$ (Table 2) are
481 deemed unreliable and omitted from figures and further discussion.

482
483 Core C1 show $\delta^{238}\text{U}_{\text{auth}}$ from $+0.25\text{‰}$ to -0.07‰ , all significantly higher than the seawater $\delta^{238}\text{U}$
484 composition of -0.39‰ and with a systematic decrease in $\delta^{238}\text{U}_{\text{auth}}$ with depth and higher $[\text{U}]_{\text{auth}}$
485 (Figures 6 and 7). The measured sediments in core C2 and at depth in core C3 show high $\delta^{238}\text{U}_{\text{auth}}$
486 similar to core C1 (Figures 6 and 7). Similarly to U, $[\text{Mo}]_{\text{auth}}$ show a progressive increase with
487 depth for core C1, with $\delta^{98}\text{Mo}_{\text{auth}}$ compositions between $+1.09\text{‰}$ and $+2.02\text{‰}$. Below ~ 20 cm the
488 $\delta^{98}\text{Mo}_{\text{auth}}$ is relatively homogenous at $\sim +1.7\text{‰}$, while above, the $\delta^{98}\text{Mo}_{\text{auth}}$ varies, including the
489 lowest $\delta^{98}\text{Mo}_{\text{auth}}$ composition at 1 cm depth ($+1.09\text{‰}$). The $\delta^{98}\text{Mo}_{\text{auth}}$ varies from $+1.85\text{‰}$ to
490 $+2.45\text{‰}$ in core C2, with samples at 37 cm and 17 cm close to the seawater $\delta^{98}\text{Mo}$ composition.
491 In core C3 the $\delta^{98}\text{Mo}_{\text{auth}}$ can only be estimated for the two deepest samples (17cm and 24 cm)
492 giving $+1.18$ and $+1.72\text{‰}$ (Figures 6 and 7).

493

494 **6.4. Evaluating the controls on the authigenic Mo and U in the Malo Jezero sediments**

495 The three water samples taken at different lake depths show both $[\text{U}]$, $[\text{Mo}]$, $\delta^{238}\text{U}$ and $\delta^{98}\text{Mo}$ very
496 close to open-ocean seawater compositions (Supplementary Information Table 5). This shows
497 that the lake is dominated by seawater-derived U and Mo, the authigenic Mo and U in sediments
498 can be directly compared to the seawater. The progressive increase in $[\text{U}]_{\text{auth}}$ and $[\text{Mo}]_{\text{auth}}$ with
499 depth in cores C1 and C2 is similar to observations in Bahamas bank carbonate sediments, where
500 $[\text{U}]_{\text{auth}}$ and $[\text{Mo}]_{\text{auth}}$ increases have been interpreted to be from increasing organic matter
501 respiration and build-up of pore-water H_2S (Romaniello et al. 2013; 2016). Cores C1 and C2,
502 however, show a clear transition around ~ 20 cm depth with a sharp increase in sedimentary
503 $[\text{Mo}]_{\text{auth}}$ and $[\text{U}]_{\text{auth}}$ as well as pore-water $[\text{H}_2\text{S}]$. This increase in $[\text{Mo}]_{\text{auth}}$ and $[\text{U}]_{\text{auth}}$ at depth could
504 be directly related *in situ* diagenetic respiration of organic matter or it may reflect an euxinic redox
505 regime in the lake with other pathways of U and Mo uptake at the time of sediment deposition
506 below ~ 20 cm depth. Correlations between $[\text{Mo}]_{\text{auth}}$ and $[\text{U}]_{\text{auth}}$ vs. C_{org} may potentially help to
507 distinguish between these two scenarios.

508

509 Positive correlations between both U vs. C_{org} and Mo vs. C_{org} have been observed in many
510 anoxic/euxinic sediments (e.g. McManus et al. 2005; Algeo and Lyons, 2006; Wagner et al. 2017).
511 The positive Mo vs. C_{org} correlation have been attributed to processes of Mo scavenging from
512 seawater by organic shuttle processes (e.g. Algeo and Lyons, 2006; Wagner et al. 2017), or,
513 alternatively, a lowering of Mo solubility in waters from microbial sulfate reduction fueling on C_{org}
514 (e.g. Helz and Vorlicek, 2019). A similar debate exist for positive U vs. C_{org} correlations, suggested
515 to either occur from direct U scavenging with organic material (e.g. Zheng et al. 2002) or C_{org}
516 fueling microbial mediated metal (and U) reduction within sediments (e.g. McManus et al. 2005;
517 Lovley et al. 1991). Available C_{org} vs. bulk $[\text{Mo}]$ and $[\text{U}]$ data for core C1, show no positive
518 correlations and little variability in C_{org} with depth (Figure 8). Similarly, no U vs. C_{org} correlation

519 have been observed in Bahamas bank carbonate sediments (Tissot et al. 2018). In contrast, the
520 four upper samples from core C1 (<20 cm) show weak negative correlations between [Mo] vs.
521 C_{org} and [U] vs. C_{org} (Figure 8), in opposite direction to general observations in euxinic basins
522 (Algeo and Lyons, 2006). If these observations are considered significant, then increased
523 microbial metal reduction leading to higher $[H_2S]$ and more efficient Mo and U uptake, while using
524 up available C_{org} in the process, could be an explanation. The lack of correlation between the [Mo]
525 vs. C_{org} in the deeper part of the core (>20cm) is consistent with the model of Helz and Vorlicek
526 (2019) suggesting [Mo] vs. C_{org} correlations degrade where the flux of Mo is independent of the
527 sulfate reduction process in strongly euxinic waters.

528

529 Yet in euxinic sediments, even minor U or Mo accumulation associated directly with organic
530 matter and/or Fe-Mn oxides, may have a significant impact on the Mo and U isotope systematics
531 as these uptake processes commonly show large isotopic fractionation (e.g. Abshire et al. 2020;
532 Barling et al. 2004; King et al. 2018; Kowalski et al. 2013). Impact of such processes in the lake
533 sediments can be investigated comparing $\delta^{98}Mo_{auth}$ and $\delta^{238}U_{auth}$ compositions to inverse $[Mo]_{auth}$
534 and $[U]_{auth}$ (Figure 9), where correlations can be attributed to mixing of different sources of
535 authigenic Mo and U. The $\delta^{238}U_{auth}$ show little variability over a range of $[U]_{auth}$, with a general
536 trend of slightly increasing $\delta^{238}U_{auth}$ with lower $[U]_{auth}$. This suggest little contribution, if any, of
537 authigenic U associated directly organic matter carrying low $\delta^{238}U_{auth}$ as observed in other anoxic
538 settings (e.g. Abshire et al., 2020; Holmden et al., 2015). Sources of authigenic U may be further
539 explored cross-plotting $\delta^{238}U_{auth}$ vs. $[U]_{auth}/C_{org}$. Here the lake sediments show a negative
540 correlation for samples with low $[U]_{auth}/C_{org}$ (<2) and $\delta^{238}U_{auth}$ decreasing from +0.2 to -0.05‰,
541 while at higher $[U]_{auth}/C_{org}$ (>2), the $\delta^{238}U_{auth}$ are similar, centered around -0.05‰ (Figure 9). This
542 relationship suggests that at high $[U]_{auth}/C_{org}$ (>2) the U uptake is dominated by *in situ* U reduction,
543 while at lower $[U]_{auth}/C_{org}$ (<2), U associated directly with organic matter constitute a significant U
544 fraction when compared to the *in situ* U reduction. This interpretation is consistent with the
545 sediment data from the Namibian shelf in Abshire et al. (2020), except that in this study the U
546 associated with organic matter has a high $\delta^{238}U_{auth}$ (~+0.2-0.4‰; Figure 9) in contrast to low $\delta^{238}U$
547 (~-0.6‰) in Abshire et al. (2020). The potential U source with such high $\delta^{238}U$, could be associated
548 with detrital, rather than authigenic, organic matter and adsorption of isotopically heavy U^{+4} before
549 transportation to the lake and sediments. Such a detrital organic U source would not be accounted
550 for in the estimated detrital U fraction and it would provide U with low $(^{234}U/^{238}U)_{act}$ and a
551 mechanism to lower estimated authigenic $(^{234}U/^{238}U)_{act}$ end-member (see section 6.2). For the Mo
552 systematics, the sediments with the lowest $\delta^{98}Mo_{auth}$ compositions also correspond to the lowest
553 $[Mo]_{auth}$ and could have significant Mo addition from organic matter and/or Fe-Mn oxides. The
554 samples with the high authigenic $[Mo]_{auth}$ below 20 cm depth in cores C1 and C2, on the other
555 hand, suggest one dominating authigenic $[Mo]_{auth}$ source (Figure 9). Cross-plotting $\delta^{98}Mo_{auth}$ vs.
556 $[Mo]_{auth}/C_{org}$ show no correlation to indicate mixing between Mo associated organic matter and/or
557 Fe-Mn oxides with low $\delta^{98}Mo_{auth}$ compared to $[Mo]_{auth}$ associated with formation and scavenging
558 of sulfidic molybdate species or $FeMoS_4$ minerals with high $\delta^{98}Mo_{auth}$ (Figure 9).

559

560 In summary, these observations suggest that the both the U and Mo uptake is primarily related to
561 microbial sulfate and metal reduction processes (and $[H_2S]$ formation for Mo) within the deeper
562 parts of cores C1 and C2. In shallower sediments with lower authigenic U and Mo uptake from

563 these processes, the role of organic matter scavenging and/or Fe-Mn adsorption for U and Mo
564 may be significant contributors to the authigenic U and Mo fractions.

565 566 **6.5. Coupled authigenic Mo and U and isotope systematics in the Malo Jezero sediments**

567 With a general understanding of the dominant uptake mechanisms for U and Mo, it offers the
568 possibility to investigate the combined behavior of the two metals in more detail (Figure 10). The
569 modest authigenic U and Mo enrichments in sediments above ~20 cm (Figure 10 and
570 Supplementary Information Table 6) is consistent with anoxia/euxinia predominantly confined to
571 the pore-water of the sediments (Tribovilliard and Algeo, 2009), while the significant increase in
572 $[Mo]_{auth}$ below ~20 cm depth (cores C1 and C2) reflect Mo and U accumulation under euxinic
573 water conditions during sediment deposition. These interpretations align well with the observed
574 changing redox regime from euxinic to oxic bottom waters in the lake over time. Based on the
575 geochemical systematics, the sediments can be divided into three zones with increasing depth: *i*)
576 a zone of Mo addition from particulate transport; *ii*) a zone of pore-water Mo and U uptake and *iii*)
577 a deeper zone of previously water column/pore-water Mo and U uptake.

578
579 Zone *i*) shows high [Fe] and [Mn] in the pore-water profiles (Figure 11) suggesting a zone of Fe-
580 Mn oxide addition and dissolution in the shallowest sediment (<1 cm depth). Pore-water [Mo]
581 surrounding these sediments are close or just below seawater [Mo] (Figure 11). Molybdenum
582 transport from an Fe-Mn particulate shuttle process (e.g. Scholz et al. 2017) is therefore a likely
583 explanation for the relatively low $\delta^{98}Mo_{auth}$ (1.02‰) in the top 1 cm sediment. However, this
584 sediment sample has relatively low $[Mo]_{bulk}$ (2.1 $\mu g g^{-1}$) and any Mo addition from Fe-Mn oxides
585 can therefore only provide a small contribution to the total accumulated Mo in the sediments as
586 also discussed in section 6.4).

587
588 Zone *ii*) the shallower <20 cm sediments in cores C2 and C1 are characterized with relatively low
589 Mo_{EF} (0.3 to 11) and U_{EF} (1.1 to 2.3) suggesting euxinic conditions localized within the pore-waters
590 (Figure 8). The $\delta^{238}U_{auth}$ (~+0.1 to +0.25‰) is consistent with the observed $\delta^{238}U$ range in modern
591 sediments with variable anoxic pore-water levels (e.g. Andersen et al. 2016). The data would be
592 consistent with permanent anoxia and a shallow oxic-anoxia boundary (low oxygen penetration)
593 in the pore-waters with authigenic U accumulation and a $\Delta^{238}U$ ~+0.6‰ (Andersen et al. 2014;
594 Figure 7), however, as discussed in section 6.4, U addition associated with organic matter may
595 also be significant. The $[Mo]_{auth}$ varies between +1.0 to +2.3‰ in the same samples. Such
596 $\delta^{98}Mo_{auth}$, lower than the seawater $\delta^{98}Mo$ composition, have been observed in reducing organic
597 carbon-rich sediments, attributed to a range of processes including low $[H_2S]$ and incomplete
598 thiomolybdate or $FeMoS_4$ transformation and, as discussed in section 6.4, addition of isotopically
599 light Mo associated with organic matter deposition or a Fe-Mn shuttle process (e.g. Azrieli-Tal et
600 al. 2013; Poulson Brucker et al. 2009; Kowalski et al. 2013; Kendall et al. 2017; Scholz et al. 2017;
601 King et al. 2018; Helz & Vorlicek, 2019). These $\delta^{98}Mo_{auth}$ compositions are similar to observations
602 in Bahamas bank carbonate sediments where the samples with the lowest pore-water $[H_2S]$ have
603 low sedimentary [Mo] and $\delta^{98}Mo$ in the range from ~-1.05‰ to ~-1.25‰ (Romaniello et al. 2016).
604 The negative [Mo] and [U] vs. C_{org} correlations suggest increased microbial sulfate reduction using
605 up available C_{org} (Figure 8), a process that fits with the increasing gradient in $[H_2S]$ with depth and
606 the observed $\delta^{238}U_{auth}$ and $\delta^{98}Mo_{auth}$ systematics. In the upper part (5 to 9 cm) with low pore-water

607 [H₂S] (0.6 to 2.1 μmol l⁻¹), the authigenic [Mo] is low, but the δ⁹⁸Mo_{auth} close to the seawater δ⁹⁸Mo
608 composition. The [H₂S] is well below the threshold (~11 μmol l⁻¹) needed for the complete
609 transformation of MoO₄²⁻ to MoS₄²⁻ (Erickson and Helz, 2000). Consequently, for this type of
610 authigenic Mo uptake, Mo is expected to be incorporated into the solid phase mostly in the form
611 of MoO₄²⁻ and this process appears to be accompanied by a low levels of Mo enrichment, but with
612 little net Mo isotope fractionation. The deeper part (13 to 17 cm) is characterized by higher
613 porewater [H₂S] (29 to 200 μmol l⁻¹) and the sediments have higher authigenic [Mo], but δ⁹⁸Mo_{auth}
614 lower than the seawater δ⁹⁸Mo composition. These observations are in accordance with previous
615 findings (Bura-Nakić et al., 2018) and could relate to the Mo isotope fractionation in the earliest
616 stages of Mo removal is significant and driven by [H₂S] near the action point of switch for complete
617 transformation of MoO₄²⁻ to MoS₄²⁻ or FeMoS₄ formation (Helz et al., 1996; Helz and Vorlicek,
618 2019; Kerl et al., 2017; Nägler et al., 2011; Tossel et al. 2005). The data within this study is
619 generally in agreement with the work of Romaniello et al. (2016) highlighting the important role of
620 [H₂S] regulating the [Mo] within the pore-waters and sedimenst. However, in contrast to the
621 observations in Romaniello et al. (2016) there is no clear trend between [Mo]_{auth} vs. δ⁹⁸Mo_{auth}, with
622 the highest δ⁹⁸Mo_{auth} recorded at a very low [Mo]_{auth} and almost in absence of pore-water [H₂S].
623

624 Zone *iii*) the high [Mo]_{auth} and [U]_{auth} below 20 cm depth in both cores C2 and C1 suggest highly
625 euxinic conditions in the lake bottom- and pore-waters during sediment deposition. Bura-Nakić et
626 al. (2018) investigated combined δ⁹⁸Mo_{auth} vs. δ²³⁸U_{auth} in another euxinic Croatian sea-water lake
627 (Rogoznica) and compared the results to organic-rich sediments from other restricted euxinic
628 basins. The deep sediments in the lake show combined δ⁹⁸Mo_{auth} vs. δ²³⁸U_{auth} systematics that are
629 broadly similar to observations from Saanich Inlet and Cariaco Basin (Figure 10). The δ⁹⁸Mo_{auth}
630 vs. δ²³⁸U_{auth} systematics of the modern euxinic basins revealed patterns that are likely to be mainly
631 controlled by interlinked factors of basin size, [H₂S] and deep-water renewal rates (Bura-Nakić et
632 al. 2018). In this framework, strongly euxinic basins with slow deep-water renewal rates, lead to
633 near quantitative Mo uptake and nearly unfractionated Mo isotope compositions in the sediments.
634 This may, for instance, be accomplished by near complete transition from molybdate to tetra-
635 thiomolybdate and effective scavenging to the sediments. In contrast, in basins with fast deep-
636 water renewal rates, less-effective Mo scavenging lead to non-quantitative removal of Mo from
637 the water column and expressed Mo isotopes fractionations in the sediments. If the transformation
638 to tetra-thiomolybdate is incomplete, Mo scavenged to the sediments will express a Δ⁹⁸Mo that
639 are ~0.7‰ lower than seawater (e.g. Bura-Nakić et al., 2018; Dahl et al., 2010; Dickson; 2017).
640 Such a scenario for the Mo accumulation could be consistent with the average δ⁹⁸Mo_{auth} of ~1.6‰
641 in the sediments below 20 cm in core C1 (Figure 7 and 10). Core C2, below 20 cm, show similar
642 behavior as core C1 for two samples, while two other samples have higher δ⁹⁸Mo_{auth} near the
643 seawater composition (Figure 7). The more variable δ⁹⁸Mo_{auth} for core C2 may be related to a
644 position closer to the lake's chemocline and variable [H₂S] in the water column. The U uptake into
645 the organic carbon-rich sediments of euxinic basins are normally less quantitative than that of Mo,
646 expressing a Δ²³⁸U of ~+0.6‰ between the reduced U in the sediments and the overlaying bottom-
647 waters (Andersen et al., 2014; Andersen et al., 2018; Bura-Nakić et al., 2018). Given a
648 predominantly U uptake from diffusion and reduction within pore-waters of the sediments, slow
649 deep-water renewal compared to U diffusion rates, may deplete U in the water column above the
650 sediments (e.g. Anderson et al., 1989; Rolison et al., 2017) and drive the waters towards lower

651 $\delta^{238}\text{U}$. The effect of slow deep-water renewal rates is that U removal becomes more quantitative
652 and the $\delta^{238}\text{U}_{\text{auth}}$ in the sediments move towards the seawater $\delta^{238}\text{U}$ composition (e.g. [Andersen](#)
653 [et al., 2014](#); [Andersen et al. 2018](#); [Bura-Nakić et al., 2018](#)). Thus, as with $\delta^{98}\text{Mo}_{\text{auth}}$, the $\delta^{238}\text{U}_{\text{auth}}$
654 data is fully consistent with bottom water euxinia in the deeper part of the lake, but with a relatively
655 fast deep-water overturning time compared to the basin size, leading to $\delta^{238}\text{U}_{\text{auth}}$ of $\sim 0\text{‰}$ in
656 sediments, $\sim 0.4\text{‰}$ higher than open ocean seawater $\delta^{238}\text{U}$ composition (Figure 7 and 10).

657
658 Similar interpretations as based on the Mo and U isotope systematics are, in principle, possible
659 to obtain from Mo vs. U enrichment factors (using Al normalization, see [Tribouillard et al. 2012](#)).
660 In this study, the Al normalization was performed using the calculated detrital $[\text{U}]/[\text{Al}]$ and $[\text{Mo}]/[\text{Al}]$
661 for each specific sample, based on the two detrital end-members (Supplementary Information
662 Table 6). It must be noted that, the large carbonate fraction in these sediments, have to be
663 considered when comparing these results to other sediments, richer in detrital siliciclastic material
664 (Figure 10). The observed $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$ for the deep part of cores C2 and C1 are about twice as high
665 as the seawater Mo/U molar ratio, a trend often interpreted as evidence for Mo addition to
666 sediments via Fe-Mn particulate shuttle processes (e.g. [Algeo and Tribouillard, 2009](#)). However,
667 similar high $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$ have also been observed for the Saanich Inlet and Cariaco Basin and the
668 combined $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$ and $\delta^{98}\text{Mo}_{\text{auth}}/\delta^{238}\text{U}_{\text{auth}}$ systematics (Figure 10) are fully consistent with
669 different Mo and U removal rates within euxinic basins with relatively fast deep-water overturning
670 rates (see [Bura-Nakić et al. 2018](#) for discussion).

671 672 **6.6. Implications for the interpretation of $\delta^{238}\text{U}$ and $\delta^{98}\text{Mo}$ in carbonate-rich sediments**

673 It is clear that the process of early diagenesis from reducing pore-water conditions within
674 carbonate-rich sediments may lead to the accumulation of authigenic U and Mo (e.g. [Romaniello](#)
675 [et al. 2013, 2016](#)). Based on Bahamas carbonate-rich sediments, [Chen et al. \(2018\)](#) and [Tissot](#)
676 [et al. \(2018\)](#) suggested a $\Delta^{238}\text{U}$ of $+0.27 \pm 0.14\text{‰}$ and $+0.24 \pm 0.06\text{‰}$, respectively, to be
677 applicable to derive seawater $\delta^{238}\text{U}$ estimates from measured bulk (anoxic) carbonate $\delta^{238}\text{U}$. The
678 $\Delta^{238}\text{U}$ of the carbonate sediments in this study were on average $+0.29 \pm 0.03\text{‰}$ higher than
679 seawater. The carbonate sediments from 1 to 17 cm depth in core C1 are interpreted to have
680 been deposited under reducing pore-waters and these samples are therefore more comparable
681 with the conditions of the Bahamas bank carbonate-rich sediments. These core C1 sediments
682 have a mean $\Delta^{238}\text{U}$ of $+0.31 \pm 0.01\text{‰}$ compared to seawater, slightly higher but within uncertainty
683 of the Bahamas carbonate-rich sediments ([Cheng et al. 2018](#); [Romaniello et al. 2013](#); [Tissot et](#)
684 [al. 2018](#)). Despite the similar $\Delta^{238}\text{U}$ at these different settings, it has to be noted that the observed
685 $\delta^{238}\text{U}$ in carbonate-rich sediments are a combination both detrital and authigenic U which may
686 have variable $\delta^{238}\text{U}$ and isotope fractionation factors (e.g. dependent on oxygen penetration
687 depth; [Andersen et al. 2014](#)). Another uncertainty is where the authigenic U is bound in the
688 sediments, as already discussed, the majority of the U is not associated with the authigenic-
689 formed aragonite in the Malo Jezero sediments. Instead it appears that the authigenic U is added
690 as U^{IV} with associated U isotope fractionation. Authigenic U addition in the Bahamas carbonate-
691 rich sediments has been suggested to be either in the form of reduced U mineral phases or
692 incorporated into the carbonate crystal lattice under anoxic conditions (e.g. [Chen et al. 2018](#)), but
693 further work is required to understand where this U^{IV} is hosted and its exact associated U isotope
694 fractionation in anoxic carbonate-rich settings.

695 Core C1 with high-resolution pore-water [H₂S] data allows to discuss the relationship between the
696 sediment [Mo] concentration and pore-water [H₂S]. The [H₂S] within the upper 17 cm is increasing
697 from 0.6 to 200 μmol l⁻¹ while the bulk sediment [Mo] increases (from 2.1 to 9.6 μg g⁻¹). Romaniello
698 et al. (2016) showed that Mo-enriched Bahamas carbonates ([Mo] 1-10 μg g⁻¹) deposited under
699 high pore-water [H₂S]_{aq} can record δ⁹⁸Mo values close to seawater. However, as observed in this
700 study and in the case of Romaniello et al. (2016), there may be an Δ⁹⁸Mo offset of ~-0.5‰ between
701 the seawater and bulk sediments even at high pore-water [H₂S]. In contrast, in Malo Jezero the
702 δ⁹⁸Mo composition is approaching seawater in the anoxic carbonate-rich sediments with low pore-
703 waters [H₂S] (<< 11 μmol l⁻¹) situated close to the sediment surface (Figure 10 and 11). A few
704 samples from core C2 are characterized with the highest δ⁹⁸Mo near the seawater composition.
705 The more variable δ⁹⁸Mo_{auth} in core C2, compared to C1, may be a consequence of the closer
706 vicinity to the chemocline in the lake and more variable redox conditions within the pore-waters.
707 However, neither pore-water [H₂S] nor other trace metal data for core C2 is available, limiting a
708 more detailed discussion. Core C3 is characterized with the lowest [Mo]_{bulk} and δ⁹⁸Mo_{bulk} and the
709 Mo is dominated by the (detrital) carbonate/dolomite fraction with a δ⁹⁸Mo near ~+1.1‰. Overall,
710 the data suggest that pore-water [H₂S] during early diagenetic processes is critical for authigenic
711 Mo uptake, as also suggested for Bahamas bank carbonate-rich sediments (Romaniello et al.
712 2016), while Mo uptake associated directly with organic matter or Fe-Mn shuttle processes appear
713 secondary in this setting. Clearly, further work is warranted to identify the link between the pore-
714 water environment, the host of authigenic Mo and isotope fractionation mechanisms in anoxic
715 carbonate-rich sediments.

716

717 **7. Conclusions**

718 The geochemistry of the carbonate-dominated sediment samples in Malo Jezero are recording
719 the significant documented changes in water column redox conditions. In the deepest part of core
720 C1 (>20 cm depth), high authigenic Mo and U accumulation are consistent with euxinic bottom-
721 water conditions during sediment deposition. Both the δ⁹⁸Mo_{auth} (~+1.6‰) and δ²³⁸U_{auth} (~-0‰) are
722 different from the seawater composition, showing similar systematics as observed in Saanich Inlet
723 and Cariaco Basin organic carbon-rich sediments. These observations are consistent with U and
724 Mo uptake from euxinic deep water and pore-water, in a basin with relatively fast deep-water
725 renewal rates. In the shallower part of the same core, both Mo and U uptake likely occurred from
726 a reducing pore-water environment leading to lower authigenic Mo and U accumulation. While
727 the δ²³⁸U_{auth} is relatively similar to the deeper section, the δ⁹⁸Mo_{auth} (1.1 to 2.3‰) is more variable,
728 primarily linked to variable pore-water [H₂S].

729

730 The results from Malo Jezero show similar δ⁹⁸Mo and δ²³⁸U as recorded within the Bahamas bank
731 carbonate-rich sediments (Chen et al. 2018; Romaniello et al. 2013; Tissot et al. 2018). The
732 results here are generally in accordance with reported shift in bulk sedimentary δ²³⁸U towards
733 higher values due to the diagenetic processes of U uptake from reducing pore-waters. The Δ²³⁸U
734 between the bulk δ²³⁸U carbonate-rich sediments and seawater (+0.31 ± 0.01‰) is slightly higher,
735 but within uncertainty of suggestions based on Bahamas samples (+0.27 ± 0.14‰ (Chen et al.
736 2018) and +0.24 ± 0.06‰, (Tissot et al. 2018)). If such a Δ²³⁸U is used as a 'correction factor' for
737 obtaining seawater compositions in paleo-redox studies, it is important to consider the exact

738 deposition environment of the samples (oxic vs. anoxic pore-waters) and that the bulk $\delta^{238}\text{U}$ is a
739 mixture of authigenic and detrital derived U. The results also suggest that $\delta^{98}\text{Mo}$ in carbonate-rich
740 sediments can, under certain conditions, be similar to seawater, however, further work is needed
741 to understand the processes controlling the $\delta^{98}\text{Mo}$ in carbonate-rich sediments and its potential
742 as a paleo-redox proxy.

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1010

1011 **Table captions (within text)**

1012 **Table 1.** Bulk sedimentary (cores C1, C2 and C3) Mo and U isotopic composition ($\delta^{98}\text{Mo}_{\text{bulk}}$ and
1013 $\delta^{238}\text{U}_{\text{bulk}}$) as well and $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ in Malo Jezero sediments.

1014 **Table 2.** Sedimentary (cores C1, C2 and C3) authigenic Mo and U compositions ($\delta^{98}\text{Mo}_{\text{auth}}$ and
1015 $\delta^{238}\text{U}_{\text{auth}}$) and concentration ($[\text{Mo}]_{\text{auth}}$ and $[\text{U}]_{\text{auth}}$) in Malo Jezero sediments.

1016

1017 **Figure captions**

1018 **Figure 1.** Location of Mljet Island, Croatia, in the Adriatic Sea and the Malo and Veliko Jezero at
1019 the western tip of the Island. The sediment sampling locations are indicated at lake depths of 30
1020 meter (core C1), 22 meter (core C2), and 13 meter (core C3).

1021

1022 **Figure 2.** Vertical distribution of trace elements (Al, Ti, Sr, V, Mo and U) in Malo Jezero sediments
1023 for cores C1 (blue triangles), C2 (green circles) and C3 (red squares). The vertical distribution of
1024 CaCO_3 content (wt%) (data for C1 core are taken from Sondi et al. (2017)) and of bulk sedimentary
1025 $\delta^{98}\text{Mo}$, $\delta^{238}\text{U}$ and $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ is also shown.

1026

1027 **Figure 3.** $[\text{Al}]_{\text{bulk}}$ vs $[\text{Ti}]_{\text{bulk}}$, $[\text{Li}]_{\text{bulk}}$, $[\text{Sr}]_{\text{bulk}}$, $[\text{Mo}]_{\text{bulk}}$, $[\text{U}]_{\text{bulk}}$, $[\text{V}]_{\text{bulk}}$ as well as $[\text{Sr}]_{\text{bulk}}$ vs $[\text{Mo}]_{\text{bulk}}$, $[\text{U}]_{\text{bulk}}$,
1028 $[\text{V}]_{\text{bulk}}$ covariation in Malo Jezero sediments for cores C1 (blue triangles), C2 (green circles) and
1029 C3 (red squares). The detrital limestone/dolomite (grey) and soil siliciclastic (yellow) end-
1030 members are marked as rhombs. The limestone/dolomite end-member represents an average of
1031 five samples while the soil-endmember is based on the *terra rossa* sample.

1032

1033 **Figure 4.** $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ covariation with $[\text{Sr}]_{\text{bulk}}$ (A) and with $1/[\text{U}]_{\text{bulk}}$ (B) for Malo Jezero sediments
1034 in cores C1 (blue triangles), C2 (green circles) and C3 (red squares). The *terra rossa* and
1035 dolomite/limestone (top sample in core C3) detrital end-members are shown as yellow and grey
1036 rhomb, respectively. The green cross is the measured $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ in the lake waters (average of
1037 1.137). Arrow represent a two-component mixing estimate.

1038

1039 **Figure 5.** Uranium (A) and Mo (B) to Al cross-plots for cores C1 (blue triangles), C2 (green circles)
1040 and C3 (red squares) and detrital dolomite/limestone 'rock' (grey rhombs) and soil '*terra rossa*'
1041 (yellow rhombs) end-members. Mixing lines between the detrital end-members are also shown.
1042 The mixing lines are used to calculate the relative authigenic vs. detrital fraction of each sample,
1043 visualized by the vertical vector line for one sample in A). Plot C) is a zoom in from B) in the lower
1044 $[\text{Mo}]$ range.

1045

1046 **Figure 6.** Depth profiles of authigenic $[\text{Mo}]$ and $[\text{U}]$ as well as the authigenic $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ for
1047 Malo Jezero sediments for cores C1 (blue triangles), C2 (green circles) and C3 (red squares).

1048

1049 **Figure 7.** The authigenic $\delta^{238}\text{U}$ vs. [U] and authigenic $\delta^{98}\text{Mo}$ vs. [Mo] for cores C1 (blue triangles),
1050 C2 (green circles) and C3 (red squares). The sediment samples from below and above 20 cm
1051 depth in cores C1 and C2, are shown as open and filled symbols, respectively. Average $\delta^{238}\text{U}$ off-
1052 sets from the seawater $\delta^{238}\text{U}$ composition for these two groups of data, are shown in the
1053 authigenic $\delta^{238}\text{U}$ vs. [U] plot.

1054

1055 **Figure 8.** Bulk [Mo] (A) and [U] (B) vs. C_{org} (wt %) correlation within core 1 (C_{org} data from Lojen
1056 et al. (2010)). The data shown no clear correlations, however the data from <20 cm show a weak
1057 negative correlation between both [Mo] (A) and [U] (B) vs. C_{org} (see text for further discussion). A
1058 similar trend in the data is observed plotting authigenic, instead of bulk, Mo and U.

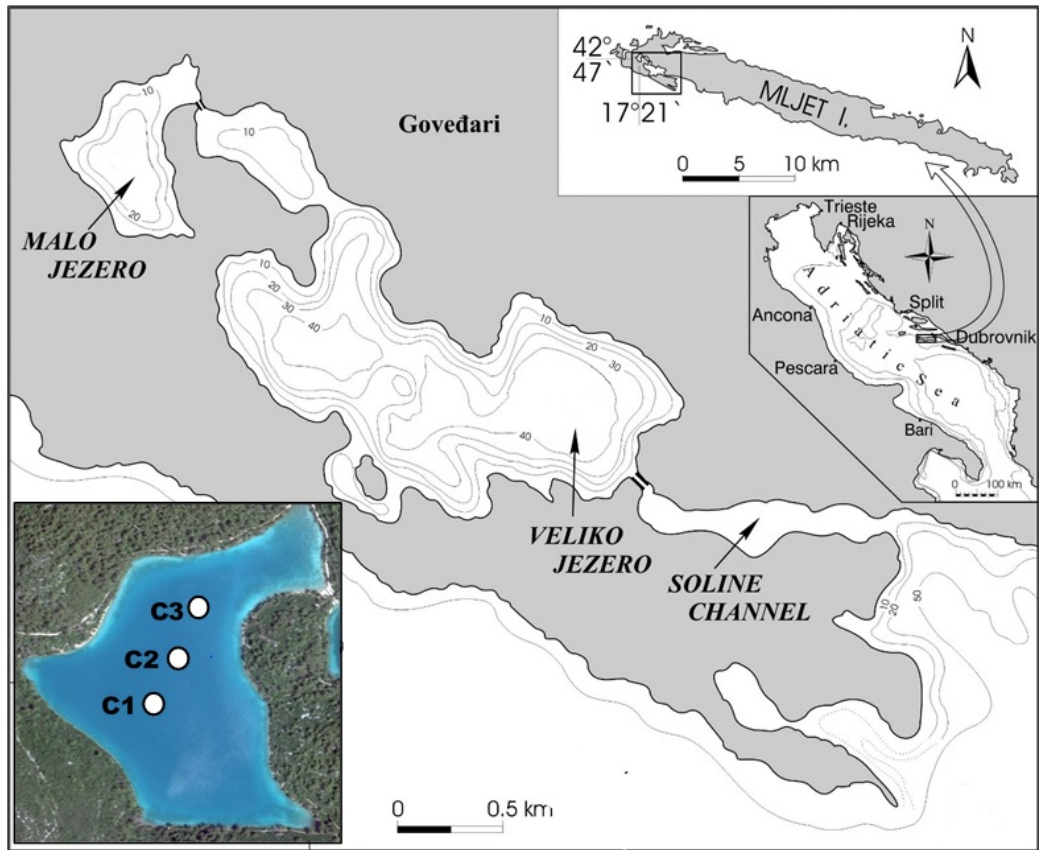
1059 **Figure 9.** Plots of $\delta^{238}\text{U}_{\text{auth}}$ vs. $1/[\text{U}]_{\text{auth}}(\text{ppm})$, $\delta^{98}\text{Mo}_{\text{auth}}$ vs. $1/[\text{Mo}]_{\text{auth}}(\text{ppm})$, $\delta^{238}\text{U}_{\text{auth}}$ vs.
1060 $[\text{U}]_{\text{auth}}(\text{ppm})/C_{\text{org}}(\text{Wt.}\%)$ and $\delta^{98}\text{Mo}_{\text{auth}}$ vs. $[\text{Mo}]_{\text{auth}}(\text{ppm})/C_{\text{org}}(\text{Wt.}\%)$. Mixing relationships between
1061 different sources of authigenic Mo and U accumulations may be expressed as linear correlations
1062 in the diagrams (see main text for further discussion).
1063

1064 **Figure 10.** U vs Mo enrichment factors (A) and authigenic $\delta^{98}\text{Mo}$ vs $\delta^{238}\text{U}$ (B) for Malo Jezero
1065 sediments compared to the average estimates of other modern euxinic basins (from Bura-Nakić
1066 et al. 2018 and references therein). The sediment samples from below and above 20 cm depth in
1067 cores C1 and C2 are shown as open and filled symbols, respectively. The grey squares represent
1068 average estimates for core C1 below (grey square with red cross) and above (grey square with
1069 blue cross) 20 cm depth, in (A) and (B). The colored circles represent sediment data from other
1070 restricted basins as labelled in diagram B. The arrows within diagram B indicates low Mo/U versus
1071 high Mo/U uptake (from Bura-Nakić et al. 2018).

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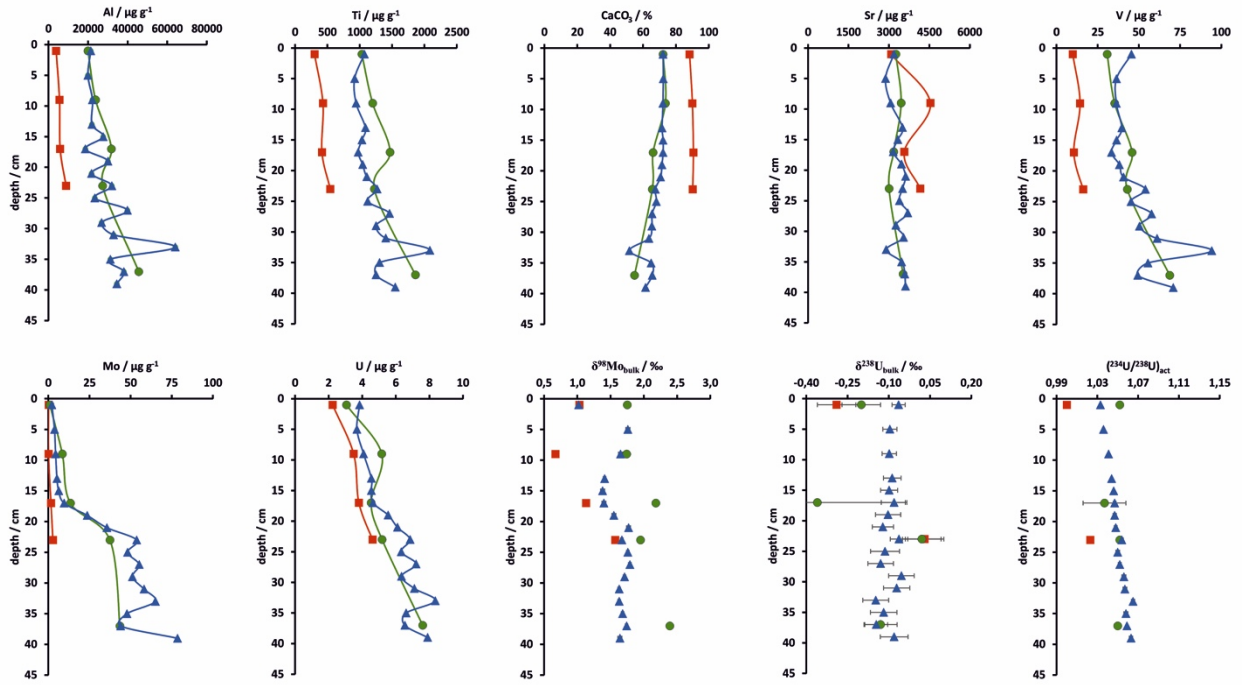
1073 **Figure 11.** Depth profiles of pore-water H_2S (orange), Mo (blue) and Fe (blue) and Mn (orange)
1074 concentrations for core C1. Depth profiles of sedimentary $\delta^{98}\text{Mo}_{\text{auth}}$ and $[\text{Mo}]_{\text{auth}}$ are also shown.
1075 In parallel is a simplified model for $\delta^{98}\text{Mo}_{\text{auth}}$ accumulation divided into the three zones: *i*) zone of
1076 Mn-oxide and Fe-oxyhydroxides dissolution; *ii*) zone of sedimentary Mo uptake from pore-waters
1077 and *iii*) zone of previous Mo uptake from within euxinic bottom-waters. Within zone *i*) the mixing
1078 of Mo sources with the different isotopic compositions may lead to low $\Delta^{98}\text{Mo}$. Zone *ii*) is
1079 characterized with shallow zone of sedimentary Mo uptake in the form of MoO_4^{2-} accompanied
1080 with minor $\Delta^{98}\text{Mo}$ and a deeper zone of the sedimentary Mo uptake accompanied with the more
1081 expressed $\Delta^{98}\text{Mo}$, likely due to the non-quantitative transformation of MoO_4^{2-} to the MoS_4^{2-} . Zone
1082 *iii*) is characterized with Mo uptake from within a euxinic water column at the time of deposition,
1083 accompanied with $\Delta^{98}\text{Mo}$ of $\sim -0.7\text{‰}$ compared to seawater (see text for further discussion).

1084



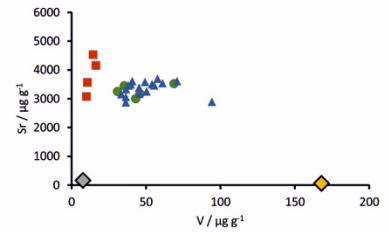
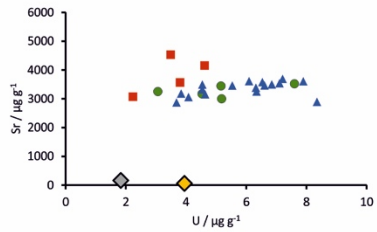
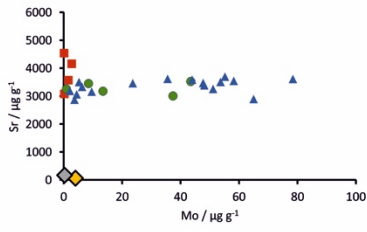
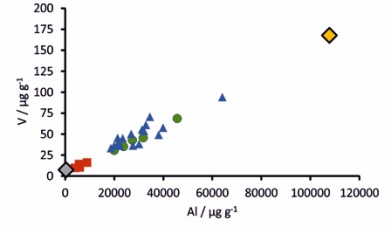
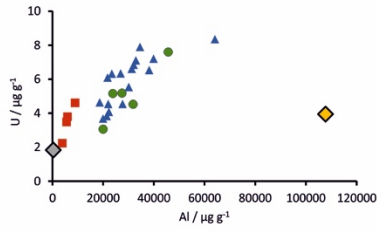
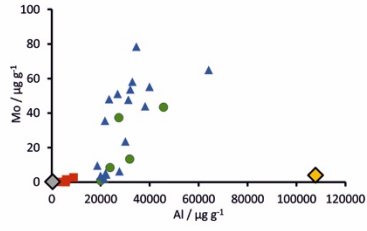
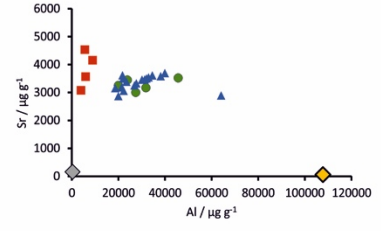
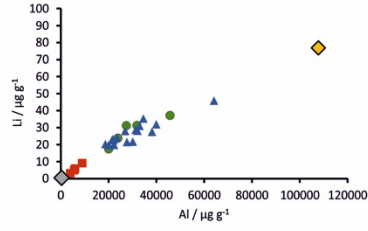
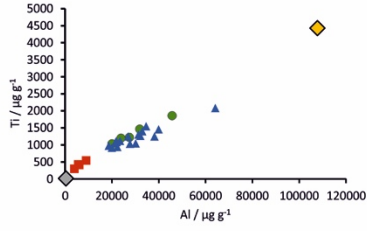
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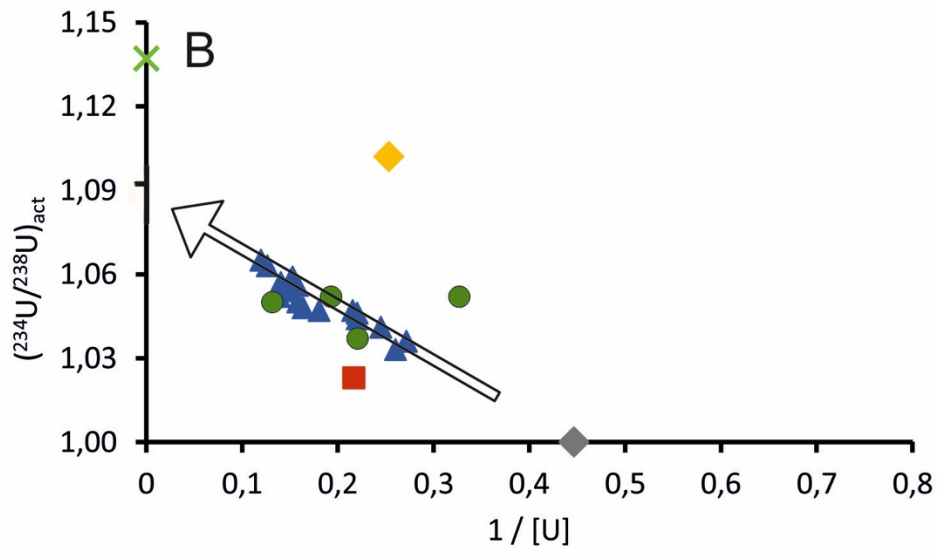
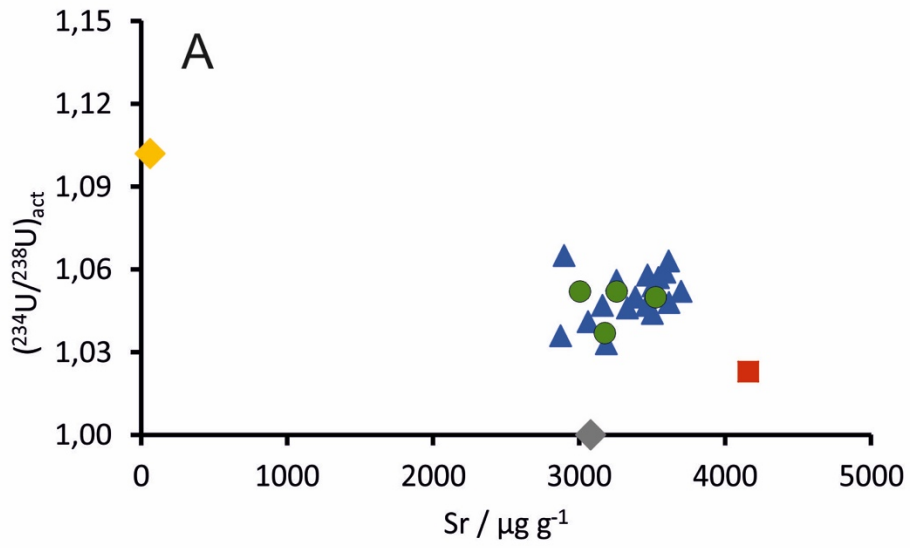
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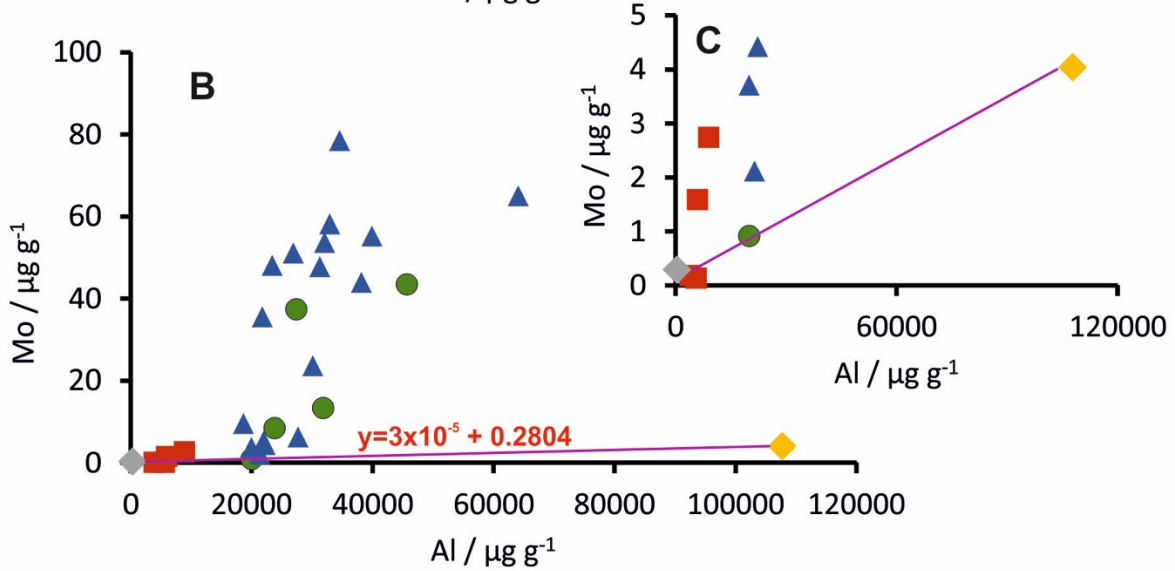
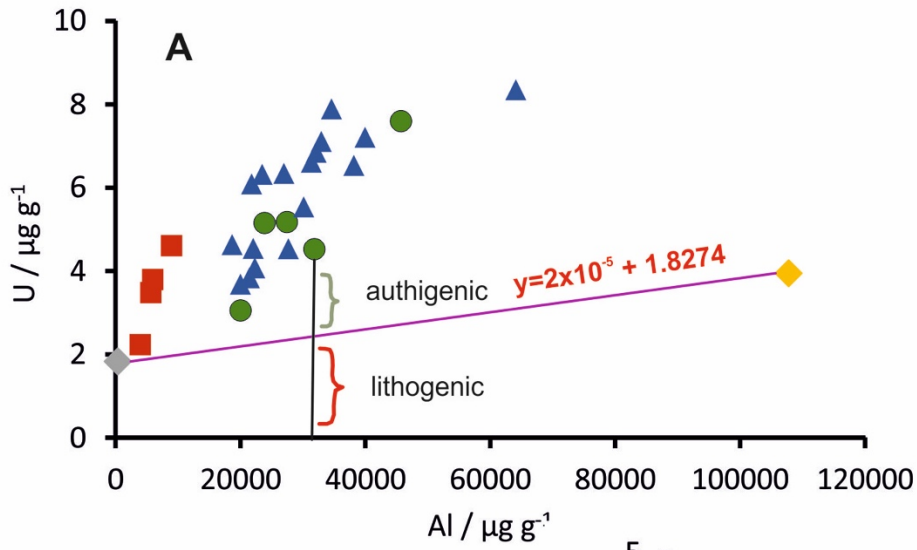
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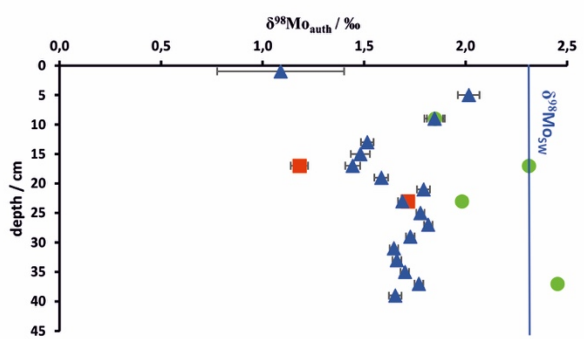
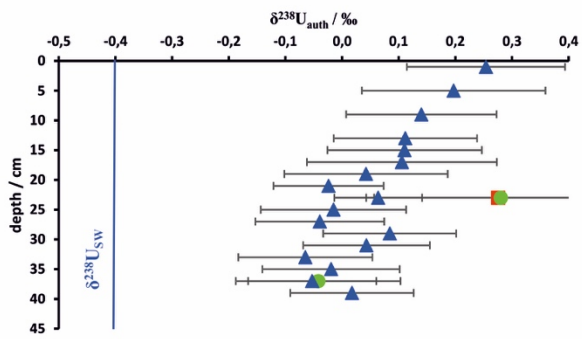
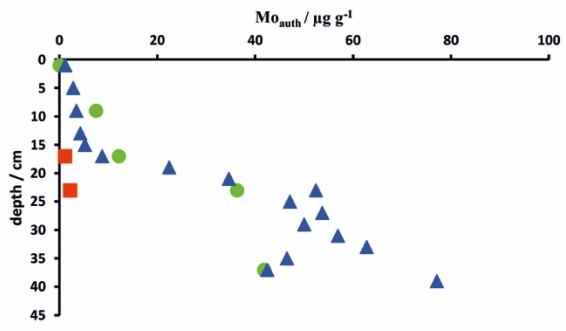
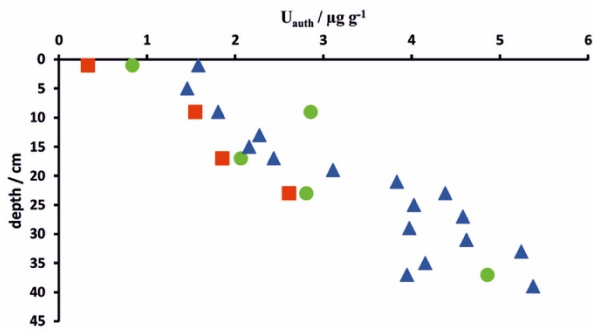
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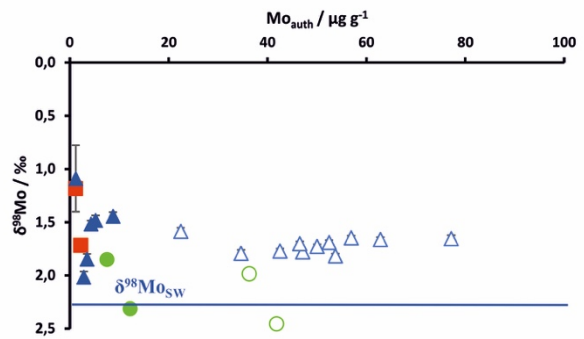
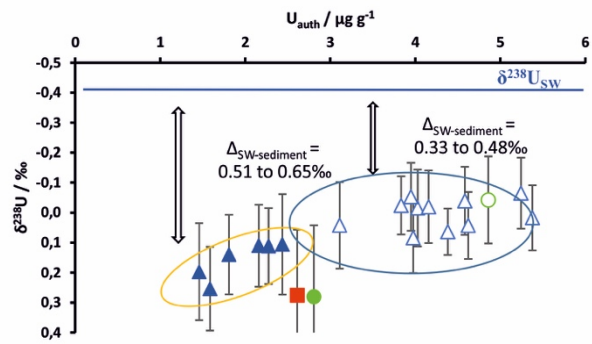
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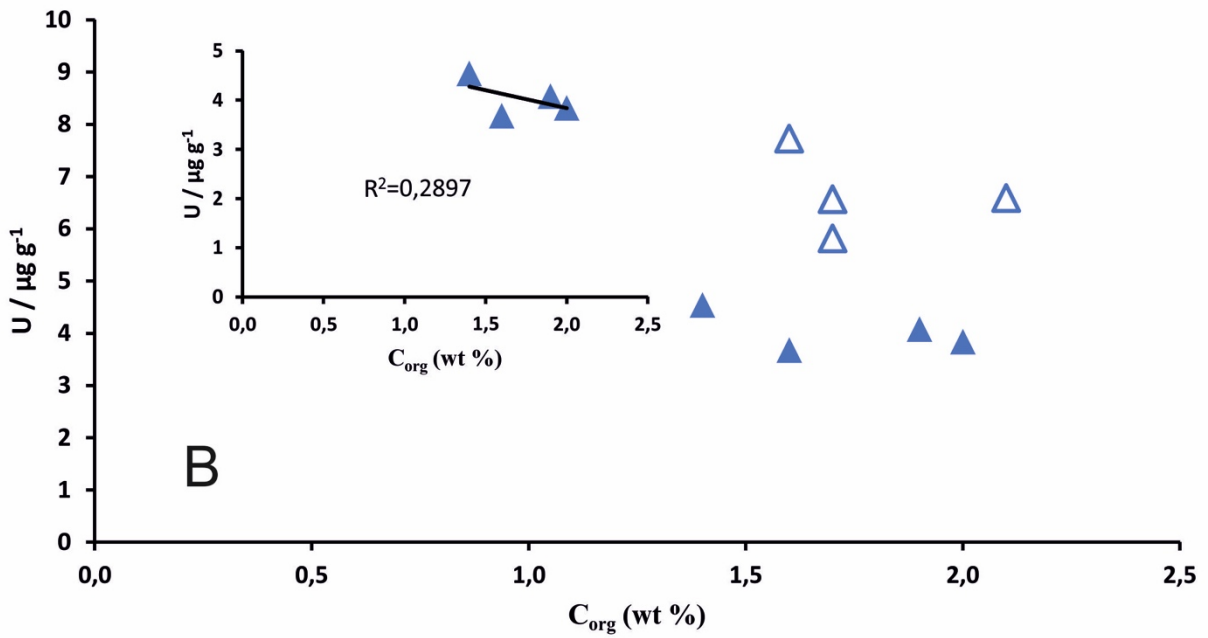
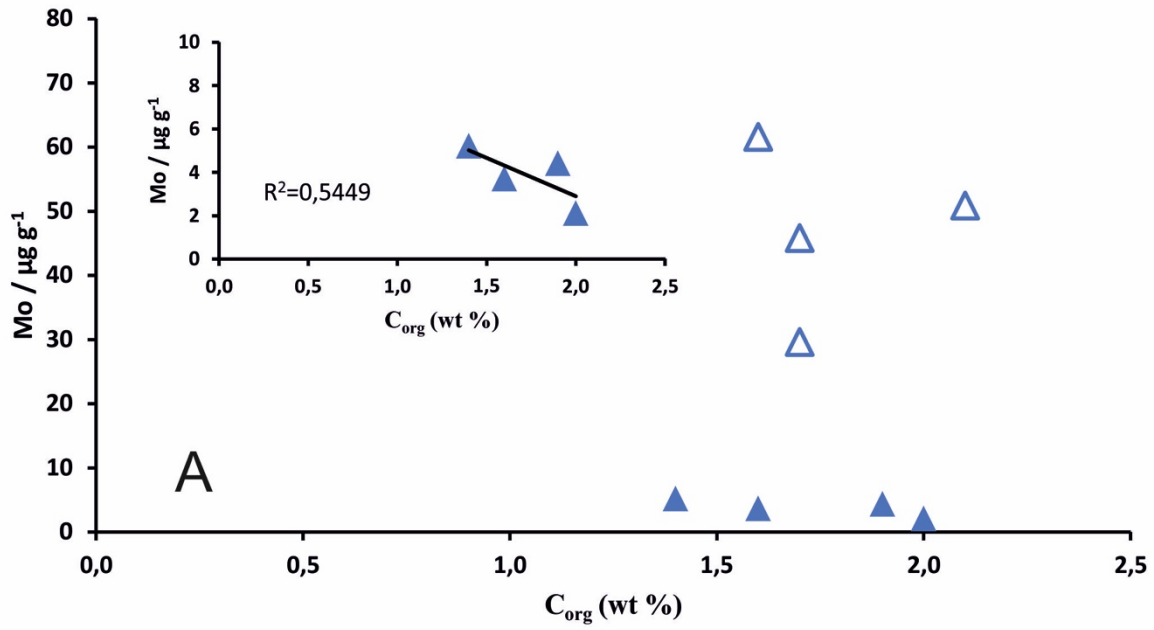
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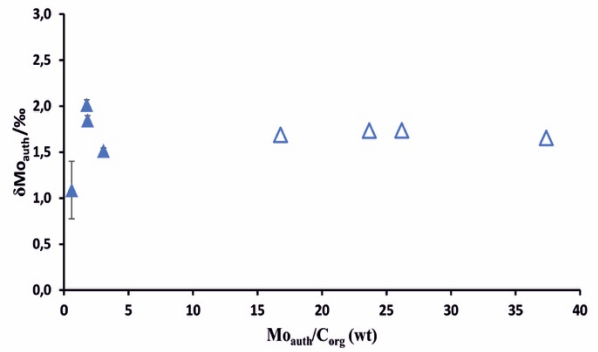
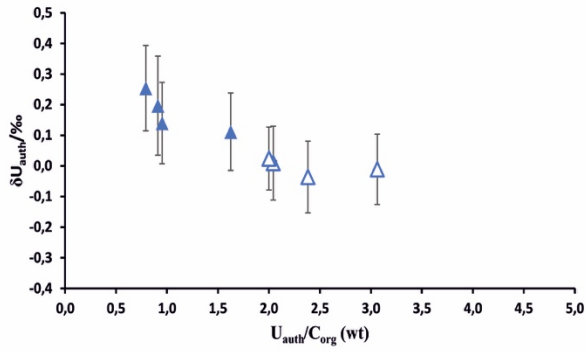
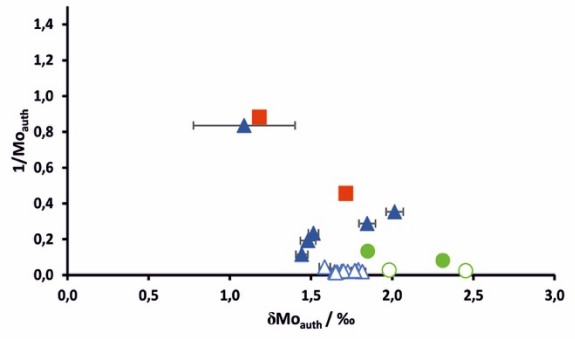
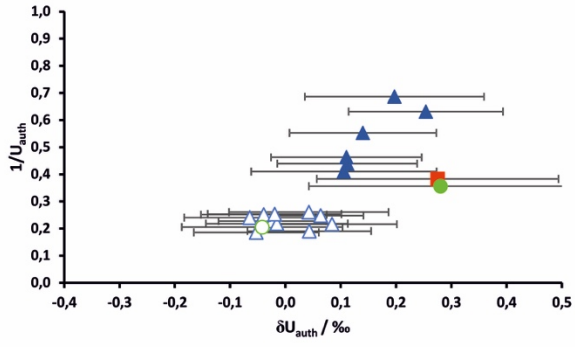
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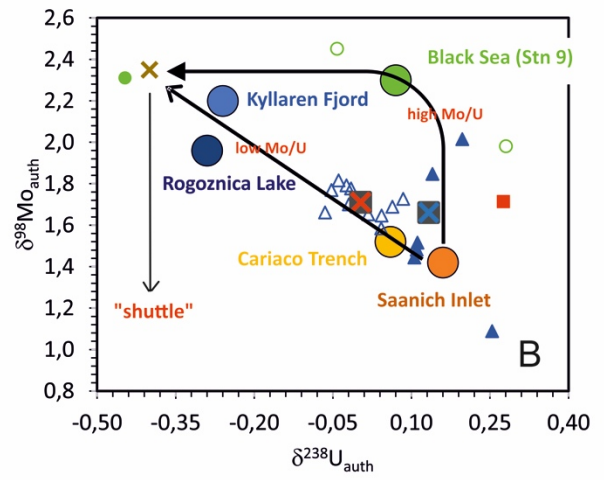
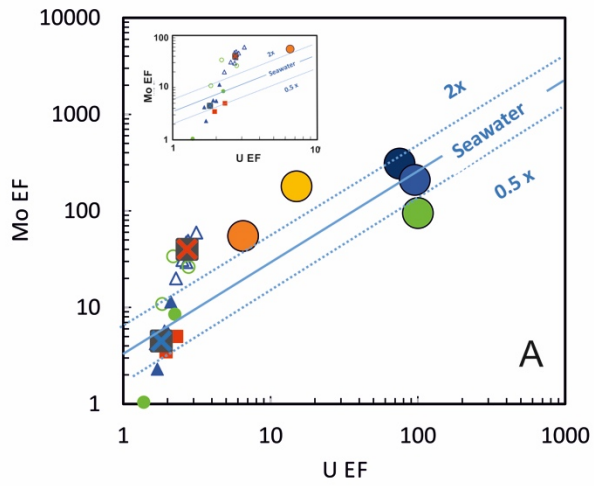
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1107 **Table 1.** Sedimentary Mo and U bulk isotopic composition ($\delta^{98}\text{Mo}_{\text{bulk}}$ and $\delta^{238}\text{U}_{\text{bulk}}$) as well
 1108 $(^{234}\text{U}/^{238}\text{U})_{\text{act}}$ in Malo Jezero sediments within cores C1, C2 and C3. The same data is given for
 1109 the catchment soil samples (*terra rossa* and humus soil).
 1110

	Depth /cm	$\delta^{98}\text{Mo}_{\text{bulk}}/\text{‰}$	$\pm 2\sigma$	$\delta^{238}\text{U}_{\text{bulk}}/\text{‰}$	$\pm 2\sigma$	$(^{234}\text{U}/^{238}\text{U})_{\text{act}}$	$\pm 2\sigma$
Core C3	1	1,03	0,05	-0,29	0,07	1,000	0,003
	9	0,67	0,07	-	-	-	-
	17	1,13	0,02	-	-	-	-
	23	1,57	0,02	0,03	0,07	1,023	0,003
Core C2	1	1,75	0,03	-0,20	0,07	1,052	0,003
	9	1,74	0,03	-	-	-	-
	17	2,18	0,02	-0,36	0,32	1,037	0,021
	23	1,95	0,02	0,02	0,07	1,052	0,003
	37	2,39	0,02	-0,13	0,06	1,050	0,003
Core C1	1	1,02	0,03	-0,06	0,02	1,033	0,000
	5	1,76	0,03	-0,10	0,03	1,036	0,001
	9	1,65	0,03	-0,10	0,03	1,041	0,001
	13	1,41	0,02	-0,09	0,03	1,044	0,001
	15	1,38	0,03	-0,10	0,03	1,046	0,001
	17	1,40	0,03	-0,08	0,05	1,047	0,001
	19	1,55	0,03	-0,10	0,05	1,047	0,002
	21	1,77	0,03	-0,12	0,04	1,048	0,001
	23	1,67	0,02	-0,06	0,03	1,054	0,001
	25	1,76	0,02	-0,11	0,05	1,050	0,002
	27	1,79	0,02	-0,13	0,05	1,052	0,001
	29	1,71	0,02	-0,05	0,05	1,056	0,001
	31	1,63	0,02	-0,07	0,05	1,057	0,002
	33	1,63	0,02	-0,15	0,05	1,065	0,002
	35	1,68	0,02	-0,12	0,05	1,058	0,002
	37	1,74	0,02	-0,15	0,04	1,059	0,000
39	1,64	0,03	-0,08	0,05	1,063	0,002	
Soil (<i>terra rossa</i>)		0,53	0,03	-0,28	0,22	1,102	0,003
Soil (humus soil)		0,62	0,04	-0,22	0,12	0,977	0,003

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1113 **Table 2.** Sedimentary Mo and U authigenic isotopic composition ($\delta^{98}\text{Mo}_{\text{auth}}$ and $\delta^{238}\text{U}_{\text{auth}}$) and
 1114 authigenic concentration ($[\text{Mo}]_{\text{auth}}$ and $[\text{U}]_{\text{auth}}$) in Malo Jezero sediments within cores C1, C2 and
 1115 C3.
 1116

	Depth / cm	$\text{U}_{\text{auth}}/\mu\text{g g}^{-1}$	$\text{Mo}_{\text{auth}}/\mu\text{g g}^{-1}$	$\delta^{238}\text{U}_{\text{auth}}/\text{‰}$	$\pm 2\sigma$	$\delta^{98}\text{Mo}_{\text{auth}}/\text{‰}$	$\pm 2\sigma$
Core C3	1	0,33	n/a*	-0,30	4,20	n/a*	
	9	1,55	n/a*	-	-	n/a*	
	17	1,85	1,13	-	-	1,18	0,04
	23	2,61	2,19	0,28	0,22	1,72	0,03
Core C2	1	0,83	0,04	0,04	0,92	20,2	19,0
	9	2,86	7,5	-	-	1,85	0,04
	17	2,07	12,2	-0,45	0,40	2,31	0,02
	23	2,81	36,3	0,28	0,24	1,98	0,02
	37	4,86	41,8	-0,04	0,14	2,45	0,02
Core C1	1	1,58	1,20	0,25	0,14	1,09	0,31
	5	1,46	2,83	0,20	0,16	2,02	0,05
	9	1,81	3,48	0,14	0,13	1,85	0,05
	13	2,27	4,29	0,11	0,13	1,52	0,03
	15	2,16	5,21	0,11	0,14	1,48	0,05
	17	2,44	8,74	0,11	0,17	1,44	0,04
	19	3,11	22,4	0,04	0,14	1,58	0,03
	21	3,83	34,7	-0,02	0,10	1,79	0,03
	23	4,38	52,4	0,06	0,08	1,69	0,02
	25	4,03	47,1	-0,01	0,13	1,78	0,02
	27	4,58	53,7	-0,04	0,11	1,82	0,02
	29	3,98	50,0	0,08	0,12	1,73	0,02
	31	4,62	56,9	0,04	0,11	1,65	0,02
	33	5,24	62,8	-0,07	0,12	1,66	0,02
	35	4,16	46,5	-0,02	0,12	1,70	0,02
	37	3,95	42,5	-0,05	0,11	1,77	0,02
39	5,38	77,2	0,02	0,11	1,65	0,03	

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1118 *The detrital fraction of $[\text{Mo}]_{\text{bulk}}$ too dominant to calculate an authigenic fraction.

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1120 **Supplementary Table 1.** H₂S concentrations in Malo Jezero water column from 1951 to 1961
 1121 (Data taken from [Buljan and Špan, 1976](#)).

Year	Date	Lake depth / m	
		20 H ₂ S / mg l ⁻¹	25 H ₂ S / mg l ⁻¹
1951	13.03.	not detected	1,86
	19.04.	not detected	3,72
	18.05.	not detected	2,21
	17.06.	not detected	2,22
	13.07.	0,61	3,31
	24.08.	0,33	2,96
	04.10.	1,32	2,73
	07.11.	not detected	2,53
	13.12.	not detected	2,35
1952	15.01.	not detected	2,88
	21.02.	not detected	4,71
	06.03.	not detected	3,88
	31.03.	not detected	3,01
	02.04.	not detected	1,93
	05.05.	not detected	3,43
	07.05.	present	2,88
	08.06.	present	present
	10.06.	present	present
	15.07.	present	present
	17.07.	present	present
	19.08.	present	present
	21.08.	not detected	present
	25.09.	not detected	present
	27.09.	not detected	3,17
	06.11.	1,28	2,33
	08.11.	not detected	traces
11.12.	4,84	4,95	
13.12.	3,83	3,68	
1953	22.01.	not detected	traces
	05.03.	not detected	2,93
	19.05.	pink water, not detected	not detected
	21.05.	pink water, not detected	not detected
	24.06.	red water, traces	no data
	14.08.	present	no data
	16.08.	present	present
	23.09.	2,93	3,21
	24.11.	not detected	0,20

1954	20.01.	not detected	not detected
	12.03.	not detected	not detected
	27.05.	not detected	not detected
	21.07.	not detected	not detected
	20.08.	not detected	not detected
	25.09.	not detected	not detected
	24.11.	not detected	1,12
1955	13.02.	not detected	not detected
	01.04.	not detected	not detected
	25.09.	present	present
1956	02.03.	not detected	1,48
1961	12.07.	not detected	not detected

1125 **Table 2.** Vertical distribution of trace elements (Al, Ti, Li, Sr, Mo, U and V) and CaCO₃ content in
 1126 Malo Jezero sediments within cores C1, C2 and C3.
 1127

Sediment	Depth /cm	Al / $\mu\text{g g}^{-1}$	Ti / $\mu\text{g g}^{-1}$	Li / $\mu\text{g g}^{-1}$	CaCO ₃ / %	Sr / $\mu\text{g g}^{-1}$	Mo _{bulk} / $\mu\text{g g}^{-1}$	U _{bulk} / $\mu\text{g g}^{-1}$	V _{bulk} / $\mu\text{g g}^{-1}$
Core C3	1	3895	301	3	88,3	3078	0,2	2,2	9,9
	9	5587	431	5	90,0	4536	0,1	3,5	14,3
	17	5926	416	6	90,6	3569	1,6	3,8	10,5
	23	8902	544	9	90,2	4158	2,7	4,6	16,2
Core C2	1	19968	1032	18	72,2	3256	0,9	3,1	30,7
	9	23808	1199	24	73,6	3451	8,5	5,2	35,3
	17	31814	1468	31	66,1	3175	13,4	4,5	45,9
	23	27404	1225	31	65,6	3004	37,4	5,2	43,0
	37	45642	1860	37	54,8	3524	43,5	7,6	68,7
Core C1	1	21403	1072	23	72,2	3185	2,1	3,8	45,5
	5	19966	921	20	72,3	2874	3,7	3,7	36,4
	9	22254	944	20	72,1	3062	4,4	4,1	36,3
	13	22011	1088	23	71,6	3501	5,2	4,5	39,6
	15	27673	1034	22	72,2	3330	6,3	4,5	36,5
	17	18641	976	20	72,2	3159	9,5	4,6	33,4
	19	30107	1044	22	71,5	3462	23,6	5,5	38,2
	21	21769	1109	23	70,7	3615	35,6	6,1	40,7
	23	32078	1268	28	67,5	3505	53,7	6,9	54,0
	25	23439	1122	24	68,1	3386	48,1	6,3	45,3
	27	39927	1460	32	65,5	3697	55,2	7,2	57,7
	29	26919	1252	28	65,4	3256	51,1	6,3	50,4
	31	32930	1402	31	63,6	3543	58,2	7,1	61,0
	33	64093	2084	46	51,7	2896	65,0	8,4	94,2
	35	31317	1306	29	64,9	3468	47,7	6,6	55,5
37	38155	1251	28	65,6	3586	43,4	6,5	49,3	
39	34548	1549	35	61,5	3613	78,5	7,9	70,8	

1128 Repeated measurements of BCR-2 gave reproducibilities better than $\pm 10\%$ (1 S.D.) and mean values
 1129 within $\pm 10\%$ of certified concentrations

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1132 **Supplementary Table 3.** Al, Ti, Li, Sr, Mo, V and U concentrations in the catchment Malo Jezero
 1133 samples.
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	Al / $\mu\text{g g}^{-1}$	Ti / $\mu\text{g g}^{-1}$	Li / $\mu\text{g g}^{-1}$	Sr / $\mu\text{g g}^{-1}$	Mo / $\mu\text{g g}^{-1}$	U / $\mu\text{g g}^{-1}$	V / $\mu\text{g g}^{-1}$
Catchment							
Host rock samples (limestone and dolomite)							
#1	192	11	0,39	125	0,20	1,3	3,5
#2	970	49	1,4	392	0,73	3,6	23,3
#3	169	9	0,27	92	0,19	1,5	3,8
#4	163	9	0,24	92	0,14	1,4	3,7
#5	174	7	0,25	121	0,20	1,4	3,5
Soil samples							
Soil (<i>terra rossa</i>)	107752	4431	77	61	4,0	4,0	168
Soil (humus soil)	53395	2323	36	102	1,4	2,4	72

1136 Repeated measurements of BCR-2 gave reproducibilities better than $\pm 10\%$ (1 S.D.) and mean values within $\pm 10\%$
 1137 of certified concentrations
 1138
 1139

1140 **Supplementary Table 4.** Pore-water Mo, U, Fe and Mn concentrations were taken from Sondi et
 1141 al. (2017) while the porewater [H₂S] was obtained within this study as described within the
 1142 'methods' section.
 1143

Pore-water	Depth / cm	Mo / nmol l ⁻¹	U / nmol l ⁻¹	Fe / nmol l ⁻¹	Mn / nmol l ⁻¹	H ₂ S / μmol l ⁻¹
C1 core	0	107	14,3	1,79	84,2	0,06
	1	86	7,1	12747	13032	0,64
	3	103	4,9	2020,16	4613,29	1,28
	5	72	4,7	1122,62	3319,99	0,00
	7	88	5,7	992,10	2998,50	2,15
	9	58	4,0	796,58	2261,15	0,42
	11	63	8,6	1094,10	1814,27	1,28
	13	70	6,6	650,21	1059,55	153
	15	71	7,0	464,56	860,72	29
	17	86	8,0	444,02	502,15	200
	19	84	8,5	440,12	306,53	284
	21	88	11,7	404,64	241,1	357
	23	73	11,2	118,93	248,19	105
	25	62	8,7	177,76	202,40	422
	27	56	8,3	47,71	128,65	430
	29	57	7,0	94,13	76,41	570
	31	62	9,3	1,79	64,47	592
	33	58	7,7	309,11	128,92	556
	35	64	9,2	1,79	43,12	584
	37	50	9,5	1,79	33,35	755
	39	76	12,1	1,79	48,10	681

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1146 **Supplementary Table 5.** Dissolved Mo and U concentrations and isotope compositions in the
1147 Malo Jezero water column (0, 12 and 25 m depth).

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Water column depth	Mo / nmol l ⁻¹	U / nmol l ⁻¹	$\delta^{98}\text{Mo}/\text{‰}$	$\pm 2\sigma$	$\delta^{238}\text{U}/\text{‰}$	$\pm 2\sigma$	$(^{234}\text{U}/^{238}\text{U})_{\text{act}}$	$\pm 2\sigma$
0 m	105.7	13.4	2,40	0,02	-0,35	0,03	1,138	0,001
12 m	110.2	13.8	2,42	0,02	-0,36	0,02	1,136	0,001
25 m	103.3	13.0	2,42	0,02	-0,37	0,03	1,137	0,001

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1156 **Supplementary Table 6.** Sedimentary lithogenic Mo and U fractions ($[Mo]_{lith}$ and $[U]_{lith}$ – estimated
 1157 using linear regression equations presented in Figure 3, Mo_{lith}/Al and U_{lith}/Al ratios and estimated
 1158 Mo and U enrichment factors (Mo_{EF} and U_{EF}).
 1159

	Depth /cm	$U_{lith} / \mu g g^{-1}$	$Mo_{lith} / \mu g g^{-1}$	$U_{lith}/Al \times 10^{-4}$	$Mo_{lith}/Al \times 10^{-4}$	U_{EF}	Mo_{EF}
Core C3	1	1,9	0,4	4,9	1,0	1,2	0,5
	9	1,9	0,5	3,5	0,8	1,8	0,3
	17	2,0	0,5	3,3	0,8	2,0	3,5
	23	2,0	0,6	2,3	0,6	2,3	5,0
Core C2	1	2,2	0,7	1,1	0,4	1,4	1,0
	9	2,3	1,0	1,0	0,4	2,2	8,5
	17	2,5	1,2	0,8	0,4	1,8	10,9
	23	2,4	1,1	0,9	0,4	2,2	33,9
	37	2,7	1,7	0,6	0,4	2,8	26,4
Core C1	1	2,3	0,9	1,1	0,4	1,7	2,3
	5	2,2	0,7	1,1	0,4	1,7	4,2
	9	2,3	1,0	1,0	0,4	1,8	4,7
	13	2,3	0,9	1,0	0,4	2,0	5,6
	15	2,4	1,1	0,9	0,4	1,9	5,7
	17	2,2	0,8	1,2	0,5	2,1	11,4
	19	2,4	1,2	0,8	0,4	2,3	20,0
	21	2,3	0,9	1,0	0,4	2,7	38,1
	23	2,5	1,2	0,8	0,4	2,8	43,2
	25	2,3	1,0	1,0	0,4	2,8	48,9
	27	2,6	1,5	0,7	0,4	2,8	37,4
	29	2,4	1,1	0,9	0,4	2,7	47,0
	31	2,5	1,3	0,8	0,4	2,7	45,9
	33	3,1	2,2	0,5	0,3	2,7	29,5
	35	2,5	1,2	0,8	0,4	2,7	39,1
	37	2,6	1,4	0,7	0,4	2,5	30,8
39	2,5	1,3	0,7	0,4	3,1	59,6	

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