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1 **Uranium isotope geochemistry in modern coastal sediments:**
2 **insights from Toulon Bay, France**

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16

17 **ABSTRACT**

18 By assessing U geochemistry as well as U isotopic composition in marine sediments (Toulon
19 Bay, NW Mediterranean Sea), authigenic U accumulation in sediments was found to be
20 tightly linked to that of Mo and V with a slight difference in accumulation rate depending on
21 sediment redox conditions and with a typical U loss in re-oxidized sediments. In sediments
22 collected on a transect along a river plume, the authigenic accumulation of these redox-
23 sensitive elements appears to be linked to the sediment grain size which probably drives the
24 redox status of the sediments. The U isotopic composition in Toulon Bay sediments showed
25 enrichment of the heavy isotope ($\delta^{238}\text{U} = -0.12 \pm 0.12 \text{ ‰}$ relative to CRM-145 in the surface
26 sediments). However, while U isotopic fractionation reaches half fractionation factor ($\Delta^{238}\text{U} =$
27 0.6 ‰) in some sediment cores, similar to typical values observed in the literature, other cores
28 show a full fractionation factor ($\Delta^{238}\text{U} = 1.2 \text{ ‰}$). In parallel, the dissolved U profiles do not
29 show a simple and typical depletion trend but rather a depletion in the top 10 cm followed by
30 release below 10 cm that is probably linked to the biotic reoxidation of authigenic U(IV). The
31 released U could be further scavenged by a competition between U-P precipitation and biotic
32 reduction which is most likely driven by diagenetic reactions via porewater acidification and
33 release of chelators and phosphorus.

34

35 **KEYWORDS**

36 Uranium; Coastal sediments; Diagenesis; Uranium isotope composition; Multiple regression

37 1. INTRODUCTION

38 The Anthropocene has been defined as the period when human (i.e., ‘anthropogenic’)
39 activities have resulted in a significant and global impact on the Earth’s climate and
40 ecosystems. These activities have grown exponentially over the last few decades and have led
41 to specific geochemical signatures, distinct from natural and long-term geological processes.
42 Understanding such processes is essential to discriminate human impacts from the natural
43 geological signature and also to predict future variations. For example, the Earth’s
44 oxygenation history is related to geochemical redox processes and so an understanding of
45 these processes is indispensable for comprehending the evolution of life (Lyons et al., 2014).
46 The exchange between the atmosphere and ocean together with seawater-sediment
47 interactions makes marine sediments a valuable archive to evaluate past conditions. The redox
48 sensitive elements (e.g., Mo, U, Re) have been used frequently as proxies of past redox
49 conditions (Holmden et al., 2015; McManus et al., 2006; Siebert et al., 2003). However,
50 further investigations on the control of geochemical processes are required in order to better
51 use such elements as paleo-proxies. Molybdenum and U exhibit conservative behavior in
52 oxygenated water (Chen et al., 1986; Collier, 1985) and exist in the dissolved oxyanion
53 (MoO_4^{2-}) or oxycation (UO_2^{2+}) forms, but are reduced and become insoluble in anoxic
54 conditions (Sundby et al., 2004; Yamada et al., 2006; Zheng et al., 2000). This specific
55 character makes their authigenic formation a potential indicator of the redox boundary.
56 Recent analytical improvements in isotope analyses have enabled the detection and
57 measurement of small variations in U isotopic compositions. As a result, monitoring the
58 $^{238}\text{U}/^{235}\text{U}$ ratio during U reduction and authigenic U formation in sediments has been used to
59 interpret redox variations in the ocean (Andersen et al., 2014; Goto et al., 2014). However, U
60 isotopic fractionation in marine conditions is still not well understood. In addition to reductive

61 reactions, other geochemical reactions such as adsorption, (co)precipitation, as well as
62 biogenic U input could contribute to the variation in isotopic U composition (Andersen et al.,
63 2014; Brennecka et al., 2011; Dang et al., 2016; Holmden et al., 2015; Stirling et al., 2015,
64 2007). Even though, *ab initio* computations and experimental experiments on U biotic
65 reduction have shown that U fractionation could reach a full fractionation factor of +1.2 ‰
66 ($\Delta^{238}\text{U}$) (Abe et al., 2008; Andersen et al., 2014; Bigeleisen, 1996; Dang et al., 2016; Fujii et
67 al., 2006; Stylo et al., 2015), most of natural sedimentary systems record only a U-half
68 fractionation factor ($\Delta^{238}\text{U}$ up to +0.6‰, Andersen et al., 2016 and references therein). Recent
69 studies suggest that a U-full fractionation factor could be observed by either a partial U
70 removal from porewater (Andersen et al., 2014) or an early U reduction in the water column
71 which is not transport-diffusion restricted (Andersen et al., 2017). However, this has been
72 only observed in ancient sediments of the Black Sea (Holocene-aged sediments, Montoya-
73 Pino et al., 2010; Weyer et al., 2008).

74 Toulon Bay (NW Mediterranean Sea) provides an interesting study site to assess the impact of
75 human activities during the Anthropocene. The ecosystem was previously found to be highly
76 contaminated by human activities, mainly due to World War II (Dang et al., 2015b; Tessier et
77 al., 2011) when Toulon Bay witnessed several battles. Previous studies on Toulon Bay
78 sediments have revealed that U, as well as Mo, Ni, Co, V and particulate organic carbon
79 (POC) showed similar behaviors (Dang et al., 2015a). Using Principle Components Analysis
80 (PCA) of 33 chemical parameters measured on 130 surface/deep sediment samples, Dang et
81 al. (2015a) showed that this group of elements was negatively correlated to the group of
82 metal/metalloid contaminants (e.g., Ag, Bi, Cd, Cu, Hg, Pb, Sn, Zn) linked to the historical
83 pollution of Toulon Bay, suggesting either different inputs to the sediments or different
84 diagenetic dynamics in the sediments. However, a better understanding of U geochemistry

85 and its isotopic composition in coastal sediments is required for more accurate paleo-
86 environmental applications.

87 The purpose of this study was to study U cycling in modern coastal sediments. The study is
88 based on a dataset including (i) U, Mo, V, POC, S, P concentrations in surface sediments (54
89 stations within Toulon Bay) as well as data from 10 additional stations where 50-cm sediment
90 cores were taken; (ii) U isotopic composition in 10 sediment cores and 10 surface samples and
91 (iii) spatial and temporal variations in U and phosphate concentrations in pore waters.

92

93 **2. MATERIALS AND METHODS**

94 **2.1. Study site and sampling**

95 The samples were collected in Toulon Bay (Fig. 1, NW Mediterranean, SE French coast),
96 which has been impacted by several anthropogenic activities including the Toulon Navy Base
97 (different sites within the harbor), yacht clubs, marinas, small urbanized river inputs and
98 aquaculture. Previous studies on Toulon Bay sediments revealed serious contamination of the
99 entire ecosystem, including the sediments, seawater and biota, e.g. mussels (Dang et al.,
100 2015a; Tessier et al., 2011). The Bay has a water residence time of 1.5 to 7.5 days (Dufresne
101 et al., 2014), low Mediterranean tide and a low input of fresh water (from the Las and
102 Eygoutier Rivers). The Bay also contains a seawall (Fig. 1) that divides it into two unequal
103 parts (a small and a large bay). The sedimentation rate in the Bay was estimated from ^{210}Pb
104 dating to be $0.21 \pm 0.05 \text{ cm y}^{-1}$ (Tessier et al., 2011).

105 With the support of the French Navy (boats, materials, divers), undisturbed surface and
106 subsurface sediments (0-5 and 5-10 cm, respectively) were collected from 54 stations situated
107 within the whole of Toulon Bay (Fig. 1) using a sediment corer (10-cm diameter and 1-m long
108 Plexiglas tube) that preserved the sediment water interface (SWI). In addition, sediment cores

109 (~50 cm long) were collected at ten specific stations (MIS, 3B, LAS0, LAS1, LAS2, LAS 3,
110 12, 15, 23 and 52, Fig. 1) in order to measure parameter depth profiles both spatially (i.e.,
111 along a pollution gradient) and temporally (i.e., seasonally).

112 Stations LAS0, LAS1, LAS2, LAS3 and 23 are situated in front of two main currently active
113 tributaries to the Bay (the Las and Eygoutier Rivers, Fig. 1); the former Las River discharged
114 close to station MIS before it was diverted. Stations MIS, 3B and 12 are located in active
115 military zones with intense ship traffic and station 15 is situated in an aquaculture area (fish
116 and mussel farming). Station 52 is located in the large bay. Samples from stations MIS, 15, 23
117 and 52 were collected in October 2009. Sediments from station 3B and LAS0-1-2-3 were
118 collected in February 2013 and May 2016, respectively. Additionally, 9 other sampling
119 campaigns were carried out at station 12, starting in April 2011 and then every 2 months from
120 May 2012 to July 2013 during which triplicate cores were obtained to determine intra-site
121 variability (Dang et al., 2014a, 2015a). Sediments were sliced every 2 cm under inert
122 atmosphere (N₂) and centrifuged (4000 rpm, 15 min, Sigma 3-18K) within 2 h of collection.
123 Pore waters were collected by filtration of the supernatant water (0.2- m in-line syringe
124 filters, cellulose acetate, Sartorius) in a N₂-purged glove box.

125 In the two tributaries (Las and Eygoutier), particle traps were set up by the IRSN
126 (Radioprotection and Nuclear Safety Institute). Five particle samples were collected during a
127 two-week period from October 2012 to May 2013, mostly during rain events (Dang et al.,
128 2015a).

129 All solid fractions were frozen (-18°C) in HDPE bottles, freeze-dried, 2-mm sieved and then
130 maintained at -18°C until further treatment (semi-total digestion and selective extraction).
131 Further details regarding sediment sampling procedures and sample preparation are detailed
132 elsewhere (Dang et al., 2015a, 2015b, 2014a, 2014b; Tessier et al., 2011).

133 **2.2. Sediment and pore water analysis**

134 A digestion was carried out on the freeze-dried sediments using aqua regia/microwave
135 digestion (see Dang et al., 2015a; Tessier et al., 2011 for further details). Total uranium
136 concentrations after digestion (2×54 surface/subsurface sediments, i.e., 0-5 and 5-10 cm,
137 respectively and ~250 core slices) and in porewaters (~ 450) were determined using HR
138 ICP/MS (Element 2, Thermo Finnigan) at the Ruđer Bošković Institute (RBI, Zagreb,
139 Croatia). Organic carbon concentrations of these sediments and soluble reactive phosphate
140 (SRP) in porewaters have been presented previously (Dang et al., 2014b) and are reported in
141 the present paper to support discussions on U geochemistry.

142

143 **2.3. U stable isotope analysis**

144 For U isotope analysis, sediments were digested and recovery was verified by analysis of
145 MESS-3 certified reference material (National Research Council of Canada). All the acid
146 solutions were double-distilled trace metal analysis grade (BDH Aristar plus; DuoPUR,
147 Milestone). The analytical procedures to determine U concentration and U isotope
148 composition were detailed in a previous study (Dang et al., 2016). Briefly, U concentration
149 was analyzed at the Water Quality Centre (WQC) at Trent University (Peterborough, Canada)
150 using an Agilent 8800 ICP/MS (Agilent Technologies, Mississauga, Canada). Chemical
151 separation of U from the matrix was performed using TRU resin (100-150 m, Eichrom). A
152 double spike technique using a mixed $^{233}\text{U}/^{236}\text{U}$ spike (IRMM-3636b) was used for internal
153 correction of instrumental mass fractionation and potential isotope fractionation on the
154 column (Stirling et al., 2007; Weyer et al., 2008). The U isotope measurements were
155 performed by MC-ICP/MS (Nu Plasma II) at the WQC. Samples were introduced using a
156 Cetac Aridus II combined with a PFA nebulizer. The U concentrations were kept at 50 ppb

157 giving a ~35 V signal on ^{238}U . The contributions of ^{235}U and ^{238}U from the double spike
158 solution are taken into account. The double spike correction was performed using the
159 exponential law. Each sample was bracketed by two double-spiked standard solutions (IRMM
160 184) and the U concentrations in samples were adjusted to $\pm 10\%$ of that in the standards.
161 Washout between samples was achieved using a 0.1 M HCl/0.3 M HF solution. Uranium
162 isotope variation in the sample ($\delta^{238}\text{U}$) is reported relative to that of the standard (IRMM-
163 184), which is defined as:

$$\delta_{IRMM-184}^{238} = \left[\frac{(^{238}\text{U}/^{235}\text{U})_{\text{sample}}}{(^{238}\text{U}/^{235}\text{U})_{IRMM-184}} - 1 \right] \times 1000$$

164 The $^{238}\text{U}/^{235}\text{U}$ ratio in the IRMM 184 was certified to be 137.697 ± 0.042 (IRMM, 2015). The
165 $^{238}\text{U}/^{235}\text{U}$ ratios measured was 137.697 ± 0.019 (2SD, n=75) using a Nu Plasma II with a
166 long-term $^{238}\text{U}/^{235}\text{U}$ ratio of 137.697 ± 0.042 (2SD, n=235). In order to compare our data to
167 other studies where CRM-145 was used as standard solution, a Δ^{238} shift of -1.102 ‰ is added
168 systematically to the $\delta_{IRMM-184}^{238}$ to convert to $\delta_{CRM-145}^{238}$. Hereafter, the data on U isotopic
169 composition are expressed relative to CRM-145.

170 3. RESULTS AND DISCUSSION

171 3.1. Uranium distribution in sediments

172 It is important to discard different phases containing U which could be detrital U (lithogenic
173 U) and U formed in situ (authigenic U) (Andersen et al., 2014). In Toulon Bay, we assume
174 that the carbonate bound U is negligible as it has been assumed for the Black Sea sediments
175 (Andersen et al., 2014; Weyer et al., 2008). Therefore, the detrital U ($\{U_{\text{detrital}}\}$) is calculated
176 based only on Al content with a detrital U/Al ratio of 1.8×10^{-5} (McManus et al., 2006;
177 Tribovillard et al., 2006):

$$\{U_{detrital}\} = U/Al_{detrital} \times \{Al\}$$

178 The difference between total U and detrital U is assumed to be the authigenic U ($\{U_{authigenic}\}$).
179 Similar calculations were made for Mo and V using detrital X/Al ratios of 1.1×10^{-5} and
180 1.63×10^{-3} ; X being Mo and V, respectively (Kyte et al., 1993; McManus et al., 2006; Morford
181 et al., 2005; Turekian and Wedepohl, 1961).

182 **3.1.1. Concentrations of total Uranium**

183 The U concentration in the surface sediments of Toulon Bay averaged $2.1 \pm 0.5 \text{ g g}^{-1}$ (n = 54,
184 Figure 1). The lowest concentrations are observed where the tributaries of the Las and
185 Eygoutier enter Toulon Bay (station LAS0-1-2-3, MIS and 23) and at the open part of the Bay
186 ($1.3 \pm 0.2 \text{ g g}^{-1}$, n = 9). This value is close to the U concentrations measured in particles from
187 the two tributaries (1.0 ± 0.2 and $2.1 \pm 0.7 \text{ g g}^{-1}$ for the Las and Eygoutier, respectively).

188 The total U profiles at ten stations (Figure 2) all show an accumulation trend in the top 10-cm
189 of the core. The uranium accumulation rate (in $\text{g U g}^{-1} \text{ cm}^{-1}$) computed by integration of U
190 concentration with depth over the first 10-cm. The values obtained (Table 1) divides the
191 stations into two groups: the first group (stations 3B, 12, 15, 52 and MIS) has a U
192 accumulation averaging $0.21 \pm 0.10 \text{ g U g}^{-1} \text{ cm}^{-1}$ while at other stations (LAS0-1-2-3 and 23),
193 only a slight U accumulation (average of $0.04 \pm 0.05 \text{ g U g}^{-1} \text{ cm}^{-1}$) was observed. It should be
194 noted that the latter five stations are situated in front of active river mouths (Las and
195 Eygoutier, Figure 1). This increasing in U concentration could be due to either a change in
196 delivered detrital U or in authigenic U accumulation. Moreover, the percentage of the
197 $U_{authigenic}$ increases with depth for all ten stations (Figure S1A), starting from different initial
198 values; $58.8 \pm 7.7 \%$ and $83.3 \pm 1.9 \%$ for the two respective groups (Table 1); higher authigenic
199 U percentages are observed for the five stations in front of the river discharge. For the group
200 including stations 3B, 12, 15, 52 and MIS, the percentage of $U_{authigenic}$ increases with depth in

201 the subsurface sediments (Figure S1A) and a correlation between total and authigenic U
202 accumulation slopes in the top 10 cm is observed (Fig. S1B). Below 10 cm, $U_{\text{authigenic}}$ reaches
203 a maximum (up to 96%). For stations LAS0-1-2-3, the $U_{\text{authigenic}}$ fraction was stable at
204 $87.2 \pm 3.0\%$ ($n = 76$) throughout the entire core, similar to the $U_{\text{authigenic}}$ fraction observed in
205 the top 15-cm of station 23 ($82.1 \pm 3.7\%$, $n = 8$).

206 The Ti/Al ratio could indicate either a change in grain size or detrital source (Morford et al.,
207 2005). The Ti/Al ratio over the whole Bay surface sediments is constant at $1.4 \pm 0.4 \times 10^{-2}$
208 ($n=54$), discounting the possibility of a drastic change in detrital source in the Bay and
209 making the Ti/Al ratio a suitable tracer of grain size. The Ti/Al ratios at ten stations are
210 constant throughout the cores (Figure 3A, Table 1) but are particularly higher (2.5 to 3.5 fold)
211 at station LAS0-1-2 (Table 1) compared to the average measured in the 54 surface sediment
212 samples, indicating coarser grain sizes in LAS0, 1, and 2 (Morford et al., 2005). Below 36 cm,
213 the Ti/Al value at station LAS2 decreased to the average seen in the Bay together with a
214 significant accumulation of U (Figure 3B). The pollution (e.g., Hg, Ag, Bi and other metals)
215 peak attributed to the World War II events (Dang et al., 2015a; Tessier et al., 2011), is deeper
216 at station LAS 2 compared to the rest of the Bay (starting at -39 cm instead of -15 cm), which
217 suggests a higher sedimentation rate at this station. The change in Ti/Al profile at station
218 LAS2 (Figure 3B) could correspond to a change in the hydrological regime of the Las River
219 which may have previously carried different types of particles. This could be attributed to the
220 reinforced concrete structure that was built to definitively divert the former Las River to the
221 current river in the 1870s (Région Provence Alpes Côte d'Azur, 2008) and/or the Dardennes
222 dam built on the upstream of the Las River in 1912 (Laliche et al., 2015). A disruption in the
223 nature of delivered particles would also alter the porosity of the sediments and induce a
224 change in U accumulation (Figure 3B).

225 At the scale of the whole bay, authigenic U, Mo, V concentrations are inversely proportional
226 to the Ti/Al ratios; this trend is more apparent at four stations in front of the Las River (Figure
227 4). This suggests that coarser sediments are not favorable for the accumulation of these redox
228 sensitive elements, probably because of enhanced diffusion of oxidizing species from
229 seawater which delay diagenetic activities (refer to the SRP profiles which will be further
230 discussed).

231 In summary, the stations situated in front of the currently active rivers (LAS0-1-2-3 and 23)
232 are different from the other stations; U accumulation is lower at the former stations (low total
233 concentration and higher contribution of detrital U) and begins closer to the sediment water
234 interface (i.e., in the first cm) than at the latter stations. This could be due to differences in the
235 input of terrestrial materials (e.g., organic matter) or a change in porosity enhancing diffusion
236 and oxygen penetration (McManus et al., 2005).

237 In deep sediments (below 15 cm), the almost constant contribution of $U_{\text{authigenic}}$ (Figure S1A)
238 shows that authigenic U is preserved in sediments, except for stations 3 and MIS. In fact,
239 previous studies have demonstrated that the sediments at stations 12, 3B and MIS have been
240 totally (the whole MIS core) or partially mixed (from -15 to -35 cm at station 3B and some
241 specific depths at station 12) during World War II events (Dang et al., 2015a, 2015b). These
242 depths correspond to a loss of authigenic U (Figure S1A) probably due to oxidation during
243 mixing events (Algeo and Maynard, 2004; Tribovillard et al., 2006). Total U profiles do not
244 show further accumulation at depth for stations 3B, 52, MIS, LAS1 and until -35 cm for
245 LAS2 (Figure 2). However, significant U accumulation is observed for stations 12, 15, 23 and
246 the bottom of the LAS2 core. The redox status of the sediments and post-depositional
247 reoxygenation would impact U geochemistry leading to the different U profiles observed in
248 these sediment cores. This will be further discussed in the following sections.

249 The authigenic U concentrations are significantly correlated to that of Mo and V (Figure S2)
250 because of their similar behavior, which is typical of redox-sensitive elements (Morford et al.,
251 2009; Sundby et al., 2004; Tribovillard et al., 2006). However, they differ in their
252 geochemistry leading to various accumulation rates depending on the redox status of the
253 depositional environment (Algeo and Maynard, 2004; Tribovillard et al., 2006). In fact, U
254 reduction leading to U accumulation involves soluble U(VI: mainly $\text{UO}_2(\text{CO}_3)_3^{4-}$) and
255 insoluble U(IV). This reduction could happen under denitrifying conditions (anoxia) (Algeo
256 and Maynard, 2004; McManus et al., 2005). However, the key step leading to Mo
257 accumulation within sediments is the sulfide activation of conservative molybdate ions to
258 reactive thio-species (Helz et al., 1996). This step is related to sulfate-reduction and then
259 favored in sulfidic conditions (Adelson et al., 2001). Vanadium accumulation in the sediments
260 results from two reduction steps ($\text{V(V)} \rightarrow \text{V(IV)} \rightarrow \text{V(III)}$). The first step begins in non-sulfidic
261 anoxic environments while the latter is fostered by free sulfide (in euxinic conditions)
262 (Tribovillard et al., 2006 and references therein).

263 Consequently, the U, Mo and V accumulate differently in the ten sediments cores when
264 compared using linear regression (Figure S2). A multiple regression model highlights the
265 relationship between the three elements (Table S1). Further details on the data treatment
266 process and its validation are shown in the Supplementary Information.

267 Four groups are revealed corresponding to four relationship equations (Figures 5, S3 and
268 Table S1). At stations 3B and MIS, a flat plane shows that authigenic U accumulation is the
269 least important when compared to that of Mo and V concentrations (low slopes of 0.03 and
270 0.01, for {U} vs Mo and V, respectively, Table S1, Figures 5 and S3). This confirms the
271 hypothesis of U loss by post-depositional reoxygenation (Algeo and Maynard, 2004;
272 Tribovillard et al., 2006) previously discussed. In the sediments at stations LAS0-1-2-3, 12,

273 52 and all surface sediments, the relationship between authigenic U and Mo was stronger than
274 that of V (slope of 0.27 and 0.05, respectively, Table S1). In fact, authigenic V, unlike
275 authigenic U and Mo, is only weakly enriched in these sediments when compared to the other
276 five stations (Figure S2). The authigenic U-Mo relationships are similar at stations 23 and 15
277 (slope of 0.45 and 0.48, respectively) while the U-V relationships are significantly different
278 (slope of 0.06 and 0.24, respectively, Figure 4, Table S1). In addition, the accumulation zone
279 of total S extends from the surface down to 15 cm for station 15 and to 30 cm for station 23,
280 corresponding to a longer anoxic-to-euxinic transition at station 23 than at 15 (Figure S4). As
281 the anoxic condition is more favorable for U and V accumulation than for Mo which is
282 accumulated in euxinic conditions only (see discussion above), the comparison among
283 $U_{\text{authigenic}}$, $Mo_{\text{authigenic}}$, $V_{\text{authigenic}}$ confirms the anoxic status at station 23 and euxinic conditions
284 at station 15. The S content in Toulon Bay (Figure S5) shows significantly higher values
285 along the coast (up to 1.9 %) than the open sea (0.38 ± 0.06 %, $n = 10$). The S accumulation
286 with sediment depth increases equally from the coast to the open sea (Figure S4), potentially
287 indicating a redox gradient.

288 To summarize, the preserved sediments could be classified on an euxinic-to-anoxic gradient:
289 15-23-52-LAS0-1-2-3. In addition, three other stations have been subjected to post-
290 depositional reoxygenation events, from minor to total mixing (12<3B<MIS) having a direct
291 impact on the redox status of the sediments.

292 **3.1.2. Uranium isotopic composition**

293 The $\delta^{238}\text{U}$ values in the top surface sediments averaged -0.12 ± 0.12 ‰ (relative to CRM-145,
294 $n=25$), close to the estimated U isotopic composition in hypoxic sediments (-0.24 ± 0.08 ‰,
295 (Andersen et al., 2016)). When compared to the value of $\delta^{238}\text{U}_{\text{seawater}}$ (-0.39 ± 0.02 ‰,
296 (Noordmann et al., 2015; Romaniello et al., 2013; Tissot and Dauphas, 2015; Weyer et al.,

297 2008), U accumulation in surface sediments would lead to an enrichment of $\Delta^{238}\text{U}_{\text{seawater-}}$
298 sediments of $0.27\pm 0.14\text{‰}$, similar to that observed in the oceanic crust (0.25‰ (Andersen et al.,
299 2016)) and carbonate sediments ($0.2\text{-}0.4\text{‰}$ (Romaniello et al., 2013)).

300 In eight stations where U isotope profiles were measured, the $\delta^{238}\text{U}$ profiles once again divide
301 themselves into 2 groups, the first group being stations 3B, 12, 15 and 52. Station 3B showed
302 an increasing $\delta^{238}\text{U}$ from a value close to that of the seawater, i.e., -0.37‰ in the surface
303 sediments to $+0.07\text{‰}$ at the bottom of the core while stations 12, 15 and 52 displayed almost
304 constant $\delta^{238}\text{U}$ profiles throughout the cores ($\delta^{238}\text{U} = -0.19\pm 0.06, -0.07\pm 0.08$ and -0.07 ± 0.04
305 ‰ , respectively) (Figure 5). These values are comparable to the profile reported for US West
306 Coast hypoxic margin sediment (Andersen et al., 2016). The second group, involving all
307 stations situated close to the river mouths, has a continuously increasing $\delta^{238}\text{U}$ signature with
308 an average of $-0.05\pm 0.07 \text{‰}$ in the surface sediments up to 0.74‰ at 40-50 cm in the core
309 (Figure 6).

310 Andersen et al. (2016) have gathered published literature on U isotopic composition and U
311 accumulation in sediments and categorized them into two main groups: “hypoxic type” and
312 “euxinic type” regarding the redox state of the water column. We have taken the Peru margin
313 sediments reported by Andersen et al. and placed them into another plot (Figure S6) as they
314 are organic-rich and seem to be strongly influenced by continental inputs-more so than two
315 other types (Andersen et al., 2016; Weyer et al., 2008). Comparing our data to these three
316 types of conditions (Figure 7A), and factoring in the oxic conditions in the water column of
317 Toulon Bay most of sediments would be categorized as “hypoxic” thus extending the range
318 of isotopic composition up to 0.8‰ .

319 Using the isotopic mass balance, the U isotopic composition in the authigenic fraction is
320 calculated, assuming a detrital U composition of -0.3 ‰ (Andersen et al., 2014), which is
321 close to the U isotopic composition of the Garonne and Rhone rivers (-0.32±0.04 ‰ and -
322 0.26±0.06 ‰, respectively (Andersen et al., 2016; Tissot and Dauphas, 2015)).

$$\delta^{238}\text{U}_{\text{authigenic}} = \frac{\delta^{238}\text{U}_{\text{bulk}} - \delta^{238}\text{U}_{\text{detrital}} \times f_{\text{detrital}}}{f_{\text{authigenic}}}$$

323 With $\delta^{238}\text{U}_{\text{bulk}}$, $\delta^{238}\text{U}_{\text{detrital}}$ and $\delta^{238}\text{U}_{\text{authigenic}}$ being the U isotopic composition of total, detrital
324 and authigenic U and f_{detrital} and $f_{\text{authigenic}}$ being the U distribution in these two fractions.

325 The $\delta^{238}\text{U}_{\text{authigenic}}$ is plotted against the $\text{U}_{\text{authigenic}}$ and compared to that in the bulk fraction
326 (Figure 7B). Three scenarios are apparent from the three lines in Figures 7B, all starting from
327 the U isotopic composition of seawater (-0.39‰). All the surface sediments, station MIS,
328 LAS1, top layer of LAS2, and 52 are not highly enriched in U (up to 3 g g⁻¹ only) but U
329 isotopes are highly fractionated. Stations 3B, 23 and the bottom layers of LAS2 display both
330 U accumulation and isotope fractionation. Sediments from stations 12 and 15 are only slightly
331 enriched in the heavy isotope but highly enriched in U. These two stations seem to be closer
332 to what has been observed in the literature with the continental conditions seen in the Peru
333 margin sediments (Andersen et al., 2016; Weyer et al., 2008). Furthermore, it should be noted
334 that the $\delta^{238}\text{U}$ values observed in Toulon Bay, mostly in stations MIS, LAS2 and 23 are the
335 highest recorded in the literature in natural sediments. That said, these values are still within
336 the theoretical range of the full U fractionation factor (+1.2‰) (Abe et al., 2008; Andersen et
337 al., 2014; Fujii et al., 2006). Andersen et al. (2014) proposed four scenarios for how
338 depositional environments would impact on U and U isotope accumulation in sediments. The
339 half U fractionation factor seems to be the consensual values recorded in marine sediments
340 worldwide (Andersen et al., 2014; Goldmann et al., 2015; Holmden et al., 2015; Montoya-

341 Pino et al., 2010; Noordmann et al., 2015; Tissot and Dauphas, 2015; Weyer et al., 2008).
342 Most of Toulon Bay sediments fall into the “oxic penetration zone” scenario defined by
343 Andersen et al. (2014) with half fractionation factor corresponding to a value of 0.2 ‰
344 (Figure 7B). In addition, a possible scenario leading to such high U isotope composition (0.2-
345 0.8‰, Andersen et al., 2014) is when U is accumulated in sediments without a full extraction
346 of U from porewater (i.e., partial U removal). A more recent hypothesis suggests that the early
347 U reduction in the floc layer above the sediments that is not transport-diffusion restricted
348 would express full isotope fractionation (Andersen et al., 2017). Both these hypotheses
349 correspond to the conditions observed at stations LAS1, LAS2, MIS and 23 (Figure 7B)
350 where sediments are submitted to a direct delivery of terrestrial materials, probably consisting
351 of coarse particles, which leads to a stronger diffusion compared to a well consolidated
352 sediment pile. Also, these sediments are either post-depositionally reoxygenated (MIS) or
353 suboxic/anoxic sediments (LAS2 and 23, see discussion above). These characteristics would
354 lead to a full fractionation factor.

355 **3.2. Uranium in pore water**

356 The concentration profiles of U and SRP in pore waters at stations 3B, 12, 15, 52, LAS2-3
357 and 23 are shown in Figures 8 and S7. The SRP results have been previously discussed (Dang
358 et al., 2015a, 2014a, 2014b) and are shown here to support the discussion on the diagenetic
359 behavior of U.

360 For all seven U profiles, typical U profiles in porewater (constant concentration or depletion
361 from porewater) (Barnes and Cochran, 1993; McManus et al., 2006; Morford et al., 2005;
362 Tribovillard et al., 2006) are observed only in the first 10 cm (Figure 8) where authigenic U
363 formation is effective (see discussion above). Below that depth, U is strongly released in
364 porewater. The high U concentration in the surface sediment porewater was attributed to

365 oxygen penetration (McManus et al., 2005); U release in deep sediments has not been
366 attributed to geochemical processes but rather to either re-oxygenation of the sediment during
367 handling or sediment oxidation by (bio)irrigation (Chaillou et al., 2002; Morford et al., 2009).
368 However, in Toulon Bay, the absence of macrofauna and plant/algae (Bernard et al., 2001)
369 discounts the contribution of bioirrigation and bioturbation (Dang et al., 2014b). Also, the
370 continuously increasing sulfide profiles with depth in these cores (Dang et al., 2015a, 2014b)
371 together with the apparent release of U in the middle of the sediment cores (Figures 8, S7)
372 exclude the hypothesis of oxygen penetration from the bottom during coring operations.
373 Therefore, the U release in deep anoxic/euxinic sediments is not a simple artefact but results
374 from a specific suite of biogeochemical processes. For example, biotic oxidation of authigenic
375 U(IV) has been shown to solubilize U (Beller, 2005; Stewart et al., 2012; Weber et al., 2011),
376 possibly from previous U accumulation in sediments due to the reduction to U(IV) minerals
377 (Algeo and Maynard, 2004; McManus et al., 2005). Also, studies have demonstrated that the
378 first 10 cm of the sediments core were controlled by Mn/Fe cycling but diagenetic products
379 (NH_4^+ , SRP, DIC, $\text{Si}(\text{OH})_4$) were strongly released below 15 cm, indicating a highly reactive
380 layer (Dang et al., 2014a, 2014b). This intense diagenesis may enhance the oxidation of
381 biogenic U(IV) either because of deviation in pH from neutral (Ginder-Vogel et al., 2010) or
382 because of an increase in U solubility by the release of potential chelators (e.g., organic matter
383 or carbonate) (Ginder-Vogel et al., 2010; Stewart et al., 2012). The observed increase in
384 soluble U is supported by the significant relationship between dissolved U and sediment U
385 (Figure 9) and highlights the redistribution between the dissolved and particulate fraction of
386 uranium.

387 The interaction between SRP and dissolved U may also influence the redistribution of U
388 between dissolved and particulate phases. The release of dissolved U in the presence of SRP

389 produces a precipitate and leads to a reduction in SRP. Thus an inverse relationship would be
390 expected between SRP and dissolved uranium. In fact, at stations 15 and 23, where SRP
391 levels are low throughout the cores dissolved U concentrations are high (up to 200-300 M
392 U) and at stations 3 and 12, SRP concentrations are inversely proportional to U, even though
393 the profiles of both elements vary within the core (Figures 8 and S7). This phenomenon as
394 well seems to be affected by seasonal variations as observed at station 12 (Figure S7): the
395 dissolved U peak at -25 cm decreases in intensity with time and with increasing SRP. At
396 stations LAS2 and LAS3, the SRP profiles support the previous hypothesis on the diagenesis
397 delay due to enhanced diffusion of oxidizing species from seawater. In fact, SRP (and
398 Si(OH)_4 , data not shown) was strongly produced below 20 cm at station LAS2 while a release
399 of these species was encountered from the SWI at station LAS3.

400 The pH profiles at six stations (3B, 12, 15, 23 and LAS2-3) highlight a clear difference
401 between 3B-12-LAS2-3 and 15-23 (Figure S8). The porewaters below the sediment/water
402 interface consistently show a lower pH value than that of the seawater (8.1-8.2). For stations
403 3B and 12, this value remains stable for the first 20 cm then markedly decreases down to 6.5
404 below 20 cm. Alternately, the porewater pH at stations 15 and 23 is constant at a value of
405 7.7 ± 0.1 (n=48) throughout the whole core. A similar trend was observed for the redistribution
406 between protein-like and humic like fluorophores at these stations (Dang et al., 2014a,
407 2014b); dominance of protein-like organic matter in the top 20 cm is followed by a switch to
408 humic-like organic matter below 20 cm at station 12, while at station 15 (sediment core
409 collected on November 2009) a dominance of protein-like organic matter occurs throughout
410 the whole core. These observations confirm strong diagenetic reactions below 20 cm at
411 stations 3B and 12, while a constant and weaker reactivity was observed at stations 15 and 23
412 (Dang et al., 2014a, b).

413 The U-P precipitation system in a seawater matrix at different pH values was modeled with
414 PHREEQC (version 2.18.3,40) similar to an approach previously described (Dang et al.,
415 2016). Briefly, the chemical speciation and the mineral saturation index in mixtures consisting
416 of U and P (in the concentration range of our samples: 1 to 500 nM and 1 μ M to 100 M,
417 respectively) in the seawater matrix was calculated (Figure S9) for a range of pH values (6-8)
418 that are relevant when considering the observed variations in the porewaters. Negative values
419 suggest that the formation of the concerned mineral is not thermodynamically favored while
420 increasing values to zero show higher potential for mineral precipitation. At the concentration
421 range found in Toulon Bay sediments, the formation of Na-autunite is more favored with a
422 decreasing pH (Figure S9); concretely speaking, U-P precipitation is more probable at stations
423 3B and 12 than at stations 15 and 23.

424 In summary, the situations in which high U release is observed (stations 15 and 23)
425 correspond to a low-to-intermediate diagenetic reactivity (i.e., lower pH, less SRP
426 production). Therefore, U removal relies only on U reduction, the intensity of which may be
427 different depending on the redox status of the sediments and on bacterial activities. Previous
428 work has demonstrated that the dissolved organic matter at station 15 is dominated by protein-
429 like fluorophores, potentially related to the location of this station near an aquaculture area
430 (Dang et al., 2014b). In the reverse case, when diagenetic activities are more intense,
431 porewater tends to be SRP-richer and decreases in pH, conditions for which the precipitation
432 of U-P mineral competes with U biotic reduction. Moreover, U-P precipitation does not
433 induce U isotopic fractionation while U biotic reduction does with a full fractionation factor
434 of 1.2 ‰ (Andersen et al., 2016; Dang et al., 2016; Stylo et al., 2015). This competition
435 between biotic reduction of U and biomineralization of U-P minerals has already been
436 observed in a previous study (Salome et al., 2013).

437

438 **4. CONCLUSIONS**

439 The dataset obtained on U isotope geochemistry permits a better understanding of U cycling
440 in modern coastal sediments. The impact of terrestrial particle size has been demonstrated to
441 be directly driving the accumulation of U, Mo and V via the redox status of the sediments.
442 Also, the impact of human activities on sediment integrity induces variations in elemental
443 geochemistry that differ from other systems where U isotopic compositions have been
444 recorded (Andersen et al., 2016 and references therein). This study has reported a full U
445 fractionation factor in modern sediments which has been previously reported only in
446 Holocene-aged sediments of the Black Sea. These data support that enhanced diffusion in
447 coarser sediments could supply a larger U amount than in a compact sediment pile and that
448 could lead to a more effective U isotope fractionation. In addition, this study reports an
449 anaerobic oxidation of authigenic U(IV) which leads to a strong release of dissolved U in
450 deep porewater. The trapping effect of SRP on the released U is attributed to strong diagenetic
451 activities leading to increasing insolubility of U-P minerals. Also, as U precipitation in
452 phosphate mineral does not induce isotopic fractionation, we suggest that the contribution of
453 SRP may alter the full U fractionation factor and SRP release is driven by the redox status of
454 the sediments (indirectly linked to diagenesis and sediment characteristics). However, further
455 studies are required to further test these hypotheses as the atypical dissolved U profiles and
456 high U isotopic composition have not been observed previously in the literature.

457

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470

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638

TABLES

Table 1: U accumulation rate (integration of U concentration with depth), percentage of authigenic U in the top surface sediments and Ti/Al ratios at ten sediment cores in Toulon Bay.

FIGURES

Figure 1: Map of the study site with the main anthropogenic activities and locations of the 54 surface (0–5 cm) sediment samples (crosses) and 10 interface sediment cores (black circles). Uranium concentrations in surface sediments of the 54 stations are also shown. White labels show surface sediments where U isotope composition was analyzed.

Figure 2: Uranium profiles in sediment cores at ten stations.

Figure 3: (A) Vertical profile of Ti/Al at ten stations, the vertical line and the grey zone indicates the average value and the range of Ti/Al for the 54 stations in the whole bay. (B) A comparison of the vertical Ti/Al ratios and total U concentrations at station LAS2.

Figure 4: Authigenic U, Mo and V concentrations vs. Ti/Al ratios in sediments at stations LAS 0-1-2-3 (green circles) and MIS, 3B, 12, 15, 23, 52 and surface sediments (blue circles).

Figure 5: A multiple regression model of authigenic U as a function of authigenic Mo and V. Four configurations are displayed and individual plots are shown in Figure S3. The r^2 values correspond to the relationship between observed vs. calculated authigenic U.

Figure 6: Vertical profiles of U isotopic composition at eight stations, the vertical line and blue zone show the value and range of $\delta^{238}\text{U}$ in seawater. The grey circles display the U isotopic profile in sediments at the US West Coast (Andersen et al., 2016).

Figure 7: (A) Total U versus U isotopic composition in Toulon Bay and also three types of sediments gathered from the literature (11 individual datasets are shown in Figure S6). (B) Uranium concentration versus U isotopic composition in the authigenic fraction (semi-filled symbols) and the bulk sediments (grey symbols) in Toulon Bay. The vertical line and blue zone display the U isotopic composition of seawater, the vertical bold line shows the full U fractionation factor from seawater ($\Delta^{238}\text{U} = 1.2 \text{ ‰}$). The two configurations: Oxidic penetration zone and Partial U porewater removal correspond to the half-U fractionation and full-U fractionation factors defined by Andersen et al. (2014)

Figure 8: Dissolved U and SRP profiles at seven stations. The grey zone at station 12 shows intra-site variation on triplicate cores while the dashed line indicates the range of seasonal variation for 10 cores. The grey zone in the U plots for stations 3B, 12 and 52 corresponds to that in stations 15, LAS2-3 and 23 to better highlight the difference in axis scaling.

Figure 9: Relationship between dissolved and total U at seven stations.

Figure 1

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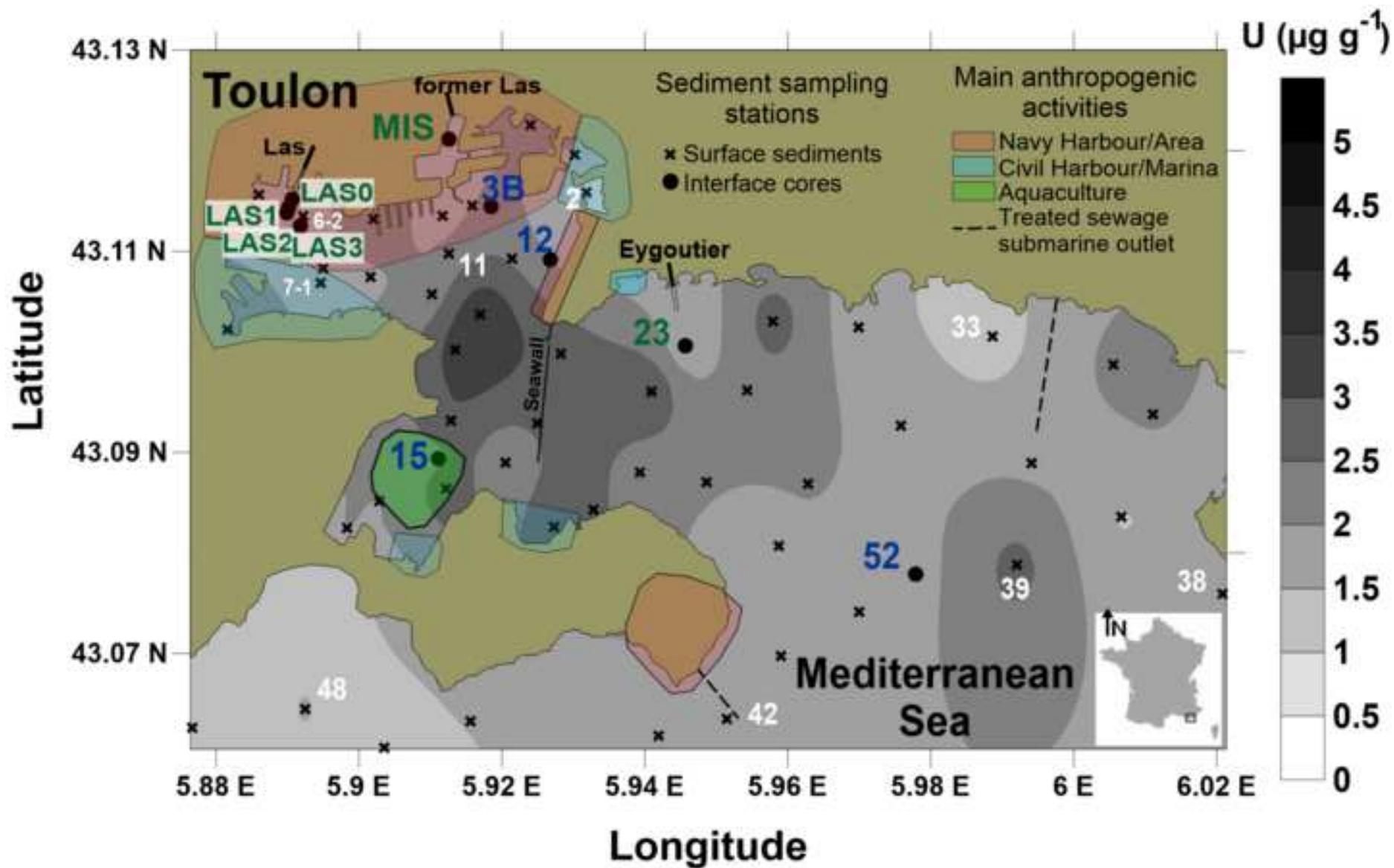


Figure 3

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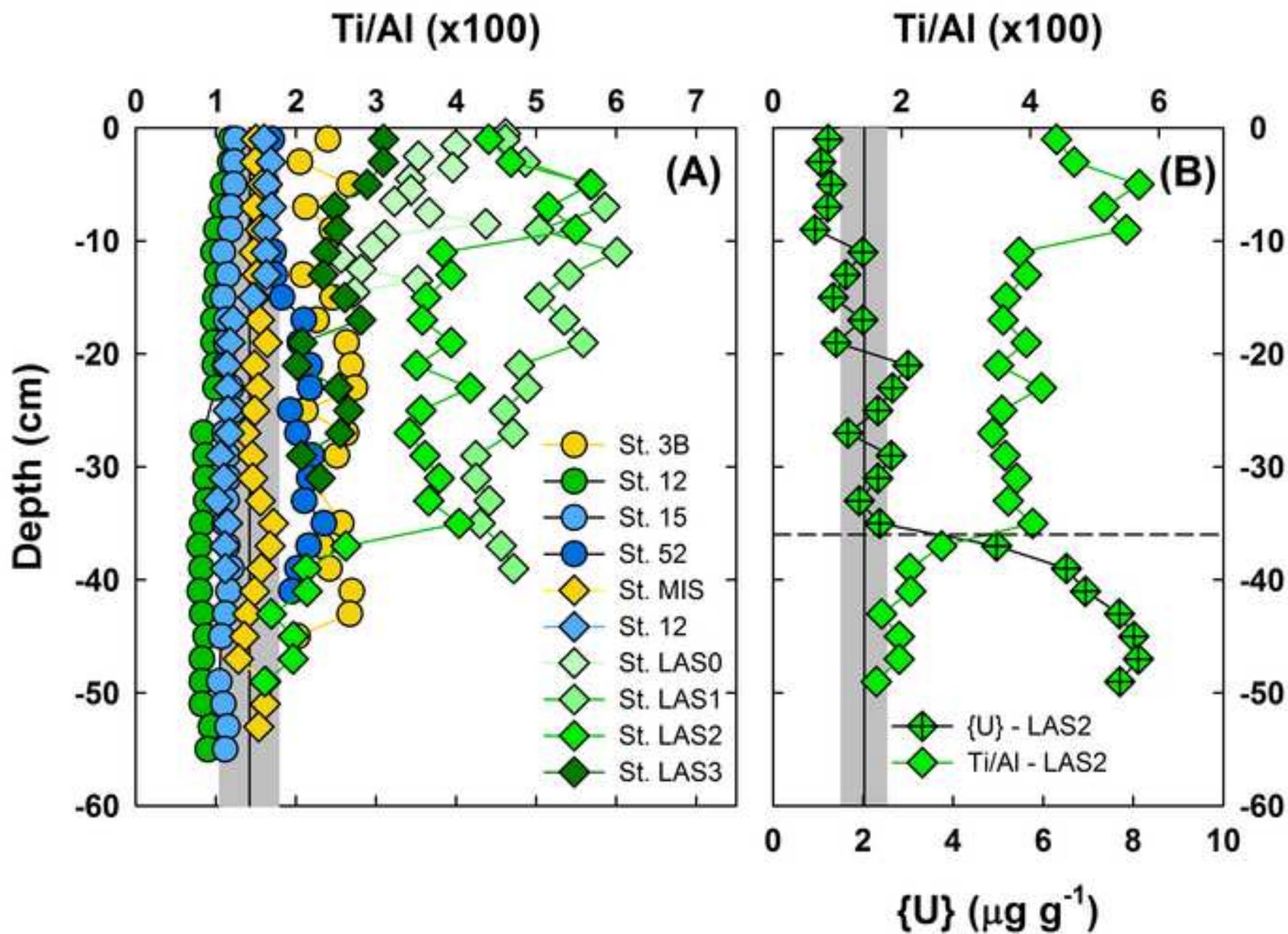


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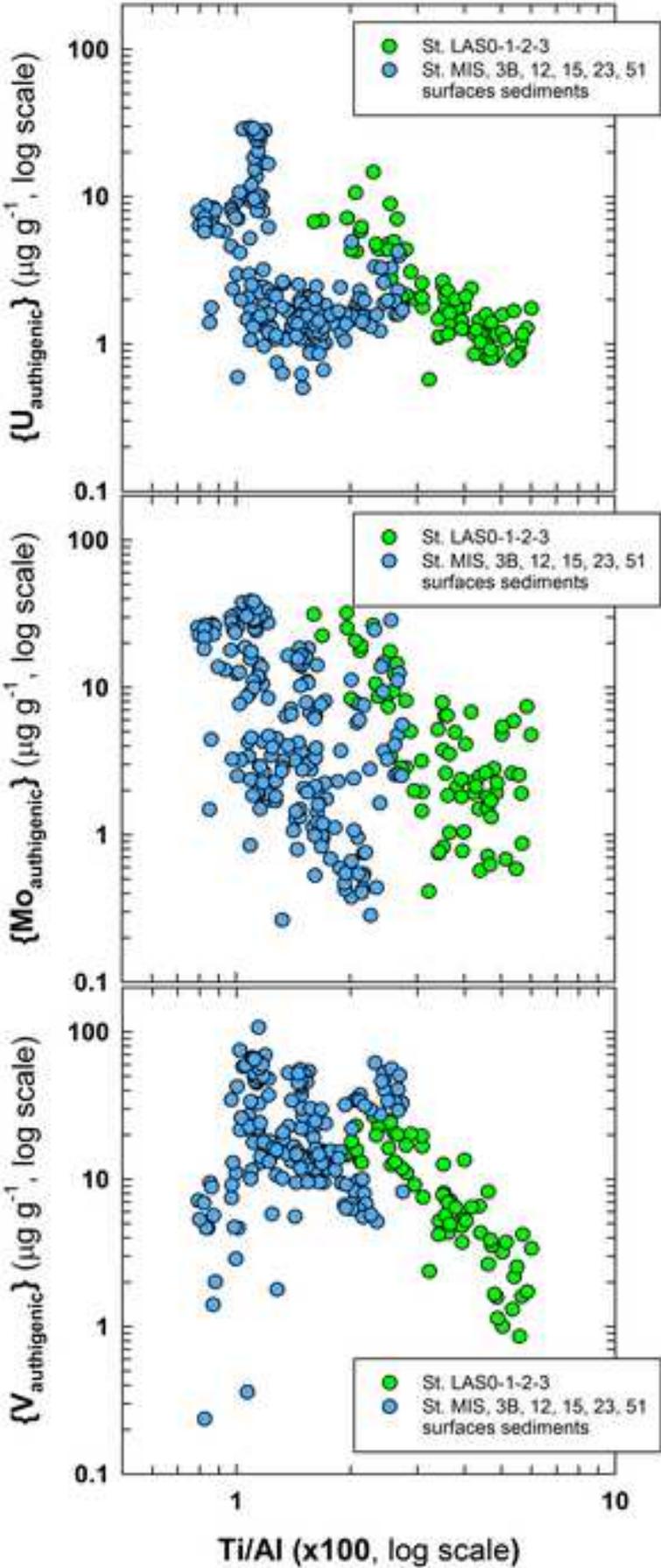


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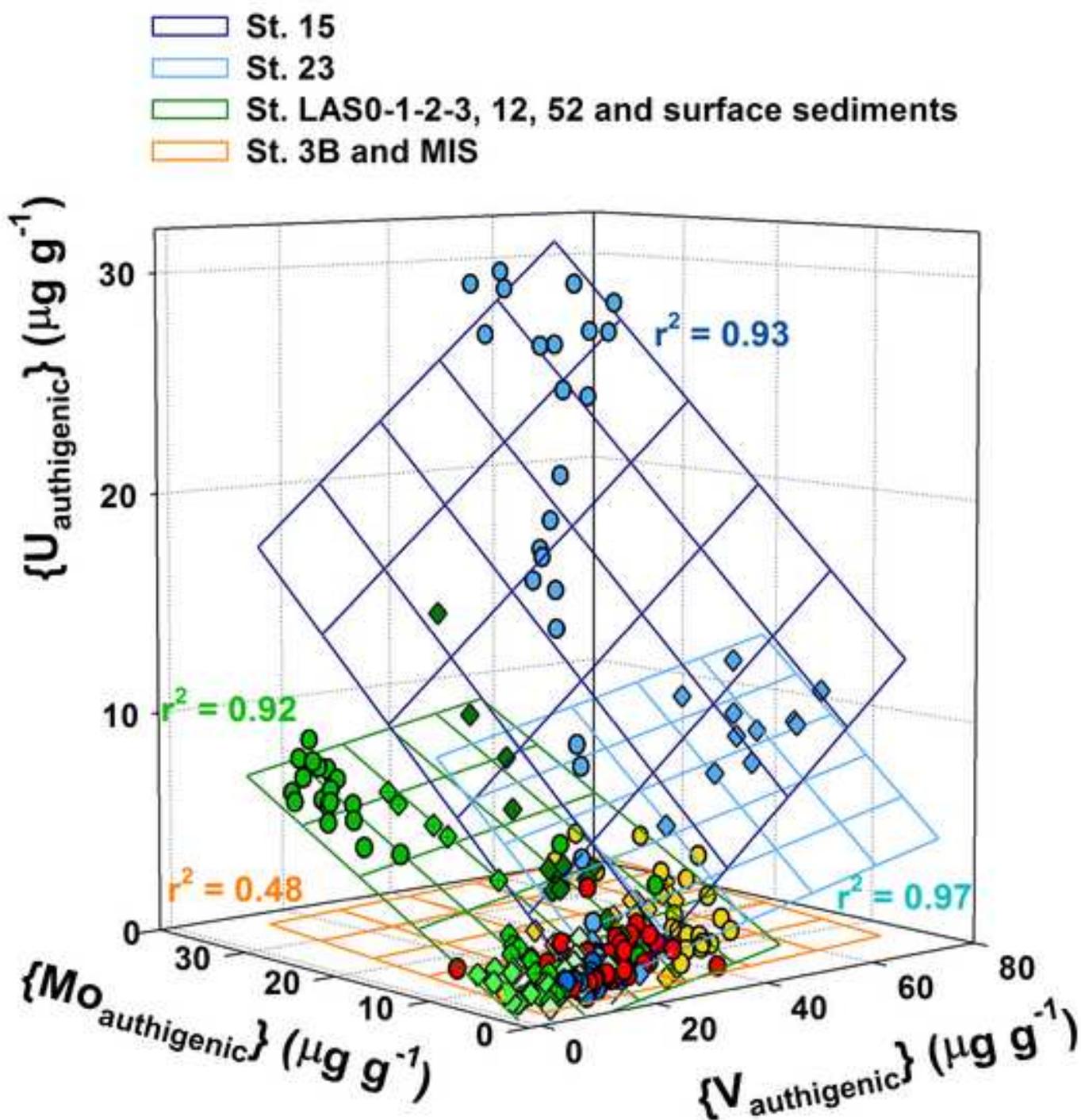


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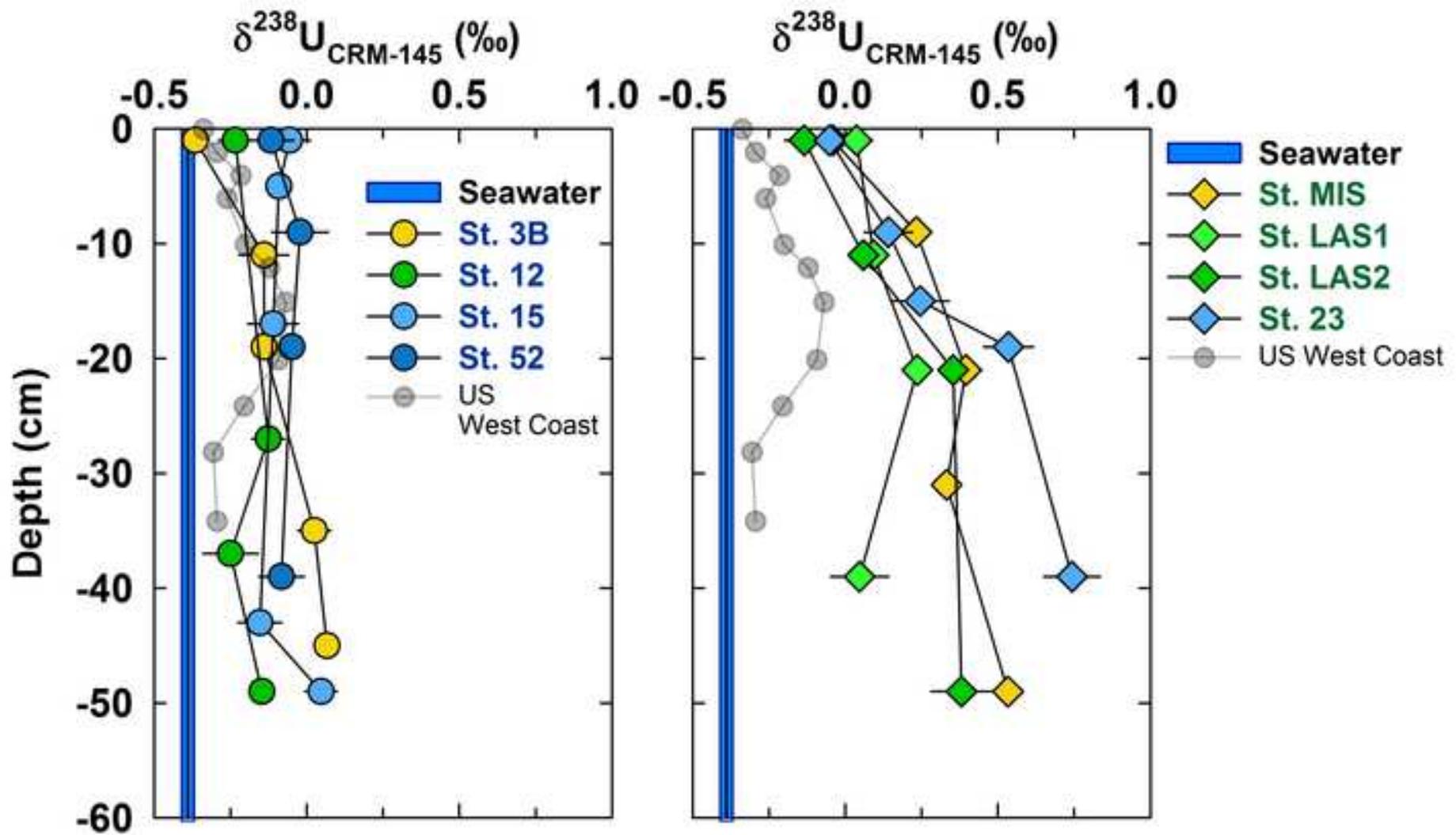


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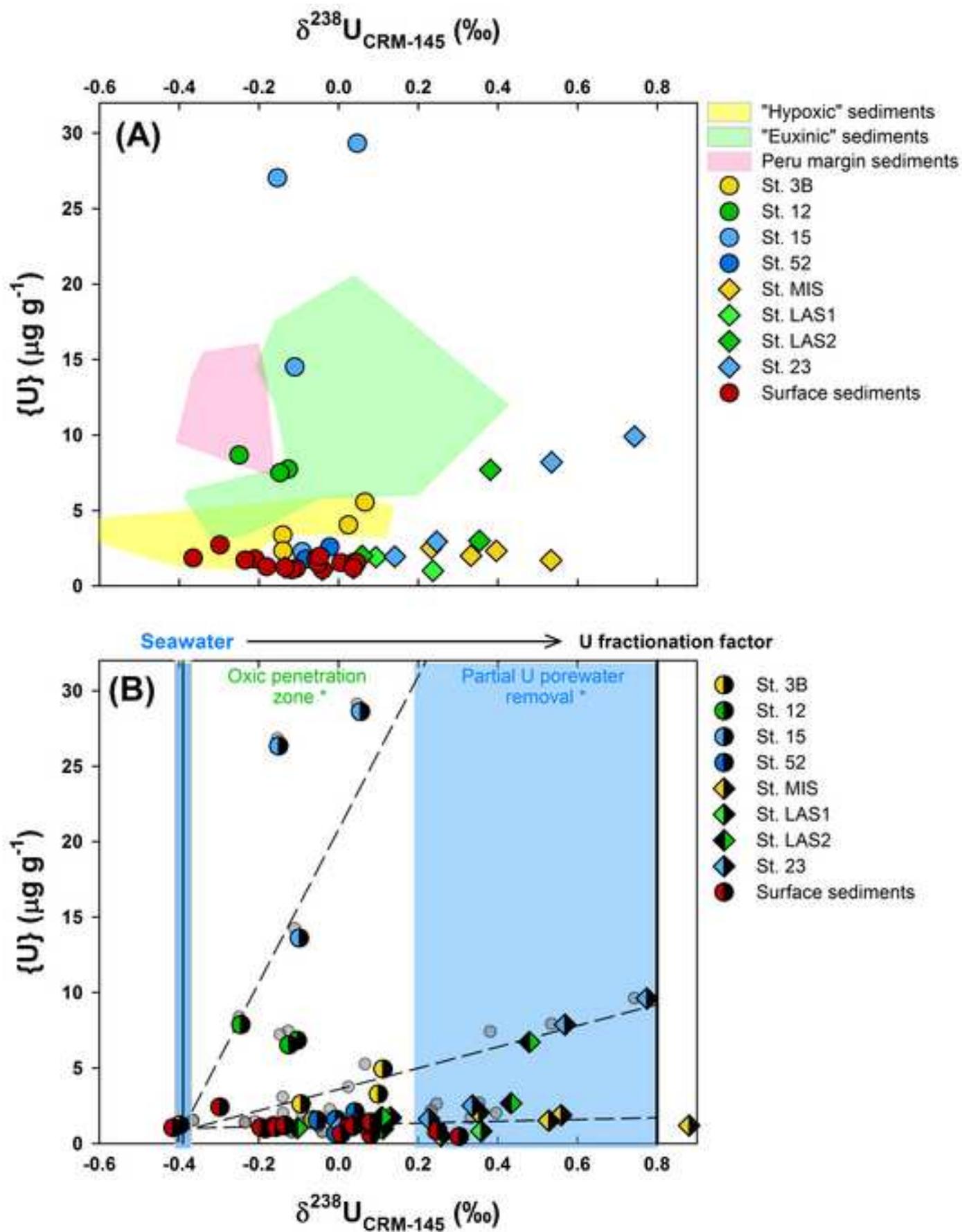


Figure 8

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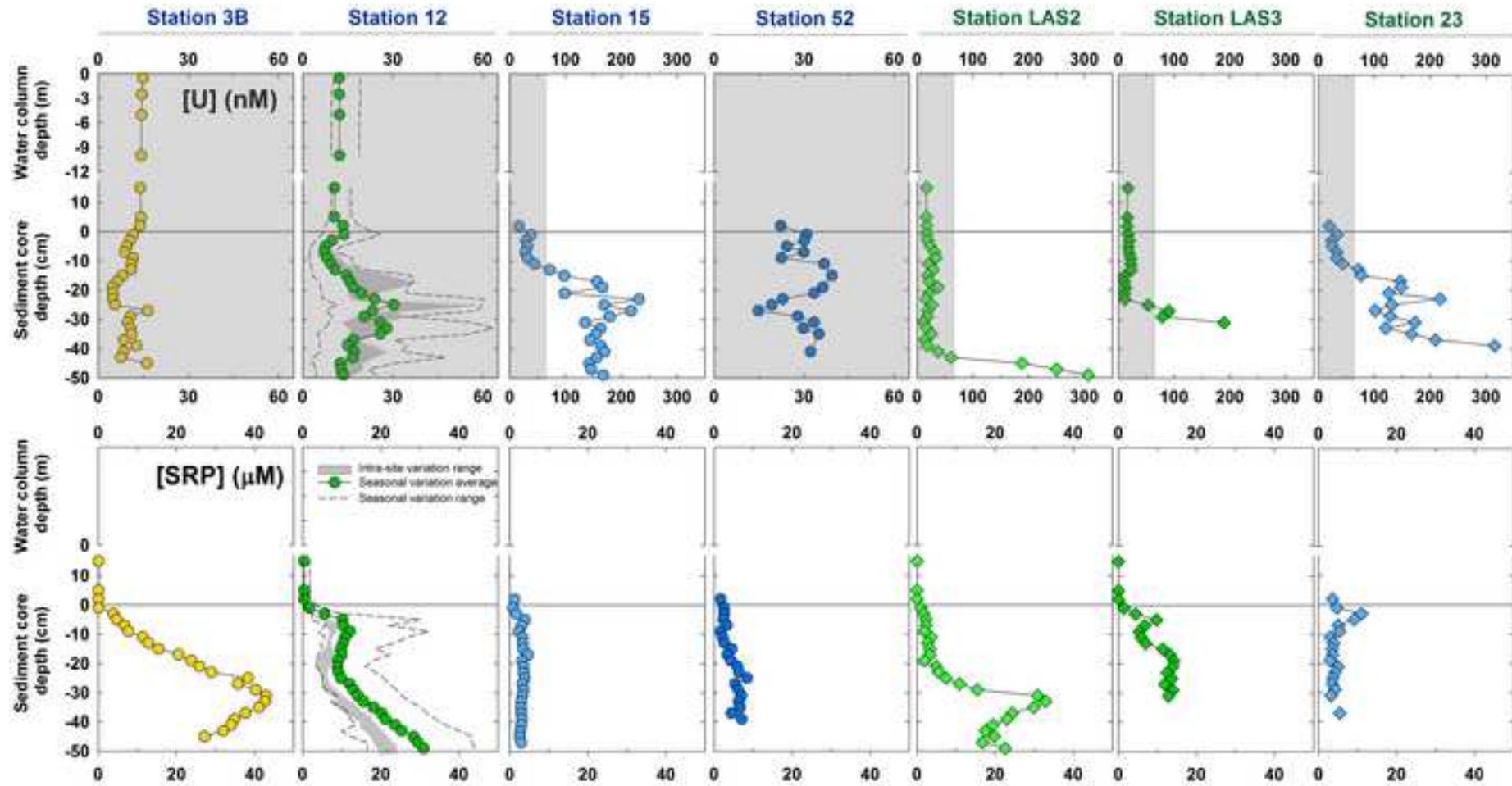


Figure 9

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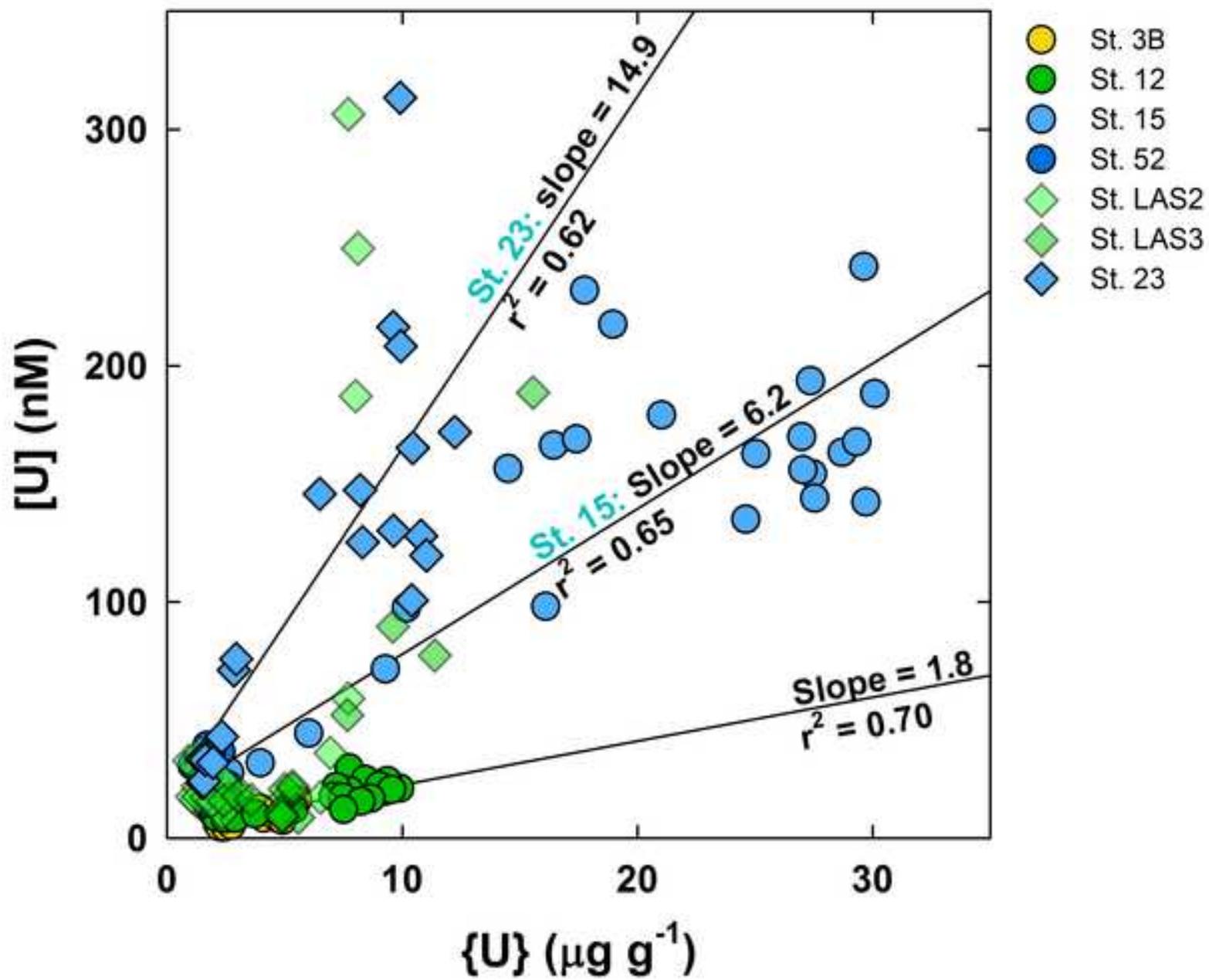


Table 1

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Table 1:

Stations	23	LAS0	LAS1	LAS2	LAS3	MIS	3B	12	15	52	
Accumulation rate ($g\ U\ g^{-1}\ cm^{-1}$) (first 10 cm)	0.03	0.10	0.06	0.0	0.4	0.19	0.17	0.24	0.14	0.13	
r^2 (linear increase in {U} with depth)	0.99	0.2	0.68	0.2	0.96	0.95	0.86	0.96	0.96	1.00	
Average		0.04 \pm 0.05					0.21 \pm 0.10				
{U _{authigenic} } (%) in 0-2 cm sediments	81.3	83.3	82.0	84.0	86.1	46.6	66.0	56.3	62.9	62.2	
Average		83.3 \pm 1.9					58.8 \pm 7.7				
Ti/Al x 100 (\pm sd)	1.3 (0.3)	3.5 (0.6)	4.9 (0.5)	3.5 (1.1)	2.5 (0.3)	1.5 (0.1)	2.4 (0.2)	0.9 (0.1)	1.1 (0.1)	1.9 (0.2)	

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