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

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ABSTRACT

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

KEYWORDS

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

1. INTRODUCTION

The Anthropocene has been defined as the period when human (i.e., ‘anthropogenic’) activities have resulted in a significant and global impact on the Earth’s climate and ecosystems. These activities have grown exponentially over the last few decades and have led to specific geochemical signatures, distinct from natural and long-term geological processes. Understanding such processes is essential to discriminate human impacts from the natural geological signature and also to predict future variations. For example, the Earth’s oxygenation history is related to geochemical redox processes and so an understanding of these processes is indispensable for comprehending the evolution of life (Lyons et al., 2014). The exchange between the atmosphere and ocean together with seawater-sediment interactions makes marine sediments a valuable archive to evaluate past conditions. The redox sensitive elements (e.g., Mo, U, Re) have been used frequently as proxies of past redox conditions (Holmden et al., 2015; McManus et al., 2006; Siebert et al., 2003). However, further investigations on the control of geochemical processes are required in order to better use such elements as paleo-proxies. Molybdenum and U exhibit conservative behavior in oxygenated water (Chen et al., 1986; Collier, 1985) and exist in the dissolved oxyanion (MoO_4^{2-}) or oxycation (UO_2^{2+}) forms, but are reduced and become insoluble in anoxic conditions (Sundby et al., 2004; Yamada et al., 2006; Zheng et al., 2000). This specific character makes their authigenic formation a potential indicator of the redox boundary. Recent analytical improvements in isotope analyses have enabled the detection and measurement of small variations in U isotopic compositions. As a result, monitoring the $^{238}\text{U}/^{235}\text{U}$ ratio during U reduction and authigenic U formation in sediments has been used to interpret redox variations in the ocean (Andersen et al., 2014; Goto et al., 2014). However, U 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; Brennecke 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

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

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

2. MATERIALS AND METHODS

2.1. Study site and sampling

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

With the support of the French Navy (boats, materials, divers), undisturbed surface and subsurface sediments (0-5 and 5-10 cm, respectively) were collected from 54 stations situated within the whole of Toulon Bay (Fig. 1) using a sediment corer (10-cm diameter and 1-m long 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).

2.2. Sediment and pore water analysis

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

2.3. U stable isotope analysis

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

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

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

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

3. RESULTS AND DISCUSSION

3.1. Uranium distribution in sediments

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

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

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

3.1.1. Concentrations of total Uranium

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

The total U profiles at ten stations (Figure 2) all show an accumulation trend in the top 10-cm of the core. The uranium accumulation rate (in $\text{g U g}^{-1} \text{ cm}^{-1}$) computed by integration of U concentration with depth over the first 10-cm. The values obtained (Table 1) divides the stations into two groups: the first group (stations 3B, 12, 15, 52 and MIS) has a U 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), 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 noted that the latter five stations are situated in front of active river mouths (Las and Eygoutier, Figure 1). This increasing in U concentration could be due to either a change in delivered detrital U or in authigenic U accumulation. Moreover, the percentage of the $U_{authigenic}$ increases with depth for all ten stations (Figure S1A), starting from different initial values; $58.8 \pm 7.7 \%$ and $83.3 \pm 1.9 \%$ for the two respective groups (Table 1); higher authigenic U percentages are observed for the five stations in front of the river discharge. For the group including stations 3B, 12, 15, 52 and MIS, the percentage of $U_{authigenic}$ increases with depth in

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

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

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

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

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

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

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

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

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

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

3.1.2. Uranium isotopic composition

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

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

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

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

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

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

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 and authigenic U and f_{detrital} and $f_{\text{authigenic}}$ being the U distribution in these two fractions.

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

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

3.2. Uranium in pore water

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

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

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

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

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

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

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

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

- Abe, M., Suzuki, T., Fujii, Y., Hada, M., Hirao, K., 2008. Ligand effect on uranium isotope fractionations caused by nuclear volume effects: An ab initio relativistic molecular orbital study. *J. Chem. Phys.* 129, 164309. doi:10.1063/1.3463797
- Adelson, J.M., Helz, G.R., Miller, C. V., 2001. Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake Bay sediments. *Geochim. Cosmochim. Acta* 65, 237–252. doi:10.1016/S0016-7037(00)00539-1
- Algeo, T.J., Maynard, J.B., 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* 206, 289–318. doi:10.1016/j.chemgeo.2003.12.009
- Andersen, M.B., Romaniello, S., Vance, D., Little, S.H., Herdman, R., Lyons, T.W., 2014. A modern framework for the interpretation of $^{238}\text{U}/^{235}\text{U}$ in studies of ancient ocean redox. *Earth Planet. Sci. Lett.* 400, 184–194. doi:10.1016/j.epsl.2014.05.051
- Andersen, M.B., Stirling, C.H., Weyer, S., 2017. Uranium Isotope Fractionation, in: Teng, F.-Z., Watkins, J., Dauphas, N. (Eds.), *Reviews in Mineralogy & Geochemistry*. pp. 799–850.
- Andersen, M.B., Vance, D., Morford, J.L., Bura-Nakić, E., Breitenbach, S.F.M., Och, L.,

488 2016. Closing in on the marine $^{238}\text{U}/^{235}\text{U}$ budget. *Chem. Geol.* 420, 11–22.
489 doi:10.1016/j.chemgeo.2015.10.041

490 Barnes, C.E., Cochran, J.K., 1993. Uranium geochemistry in estuarine sediments: Controls on
491 removal and release processes. *Geochim. Cosmochim. Acta* 57, 555–569.
492 doi:10.1016/0016-7037(93)90367-6

493 Beller, H.R., 2005. Anaerobic, nitrate-dependent oxidation of U (IV) oxide minerals by the
494 chemolithoautotrophic Bacterium *Thiobacillus denitrificans*. *Appl. Environ. Microbiol.*
495 2170–2174. doi:10.1128/AEM.71.4.2170

496 Bernard, G., Denis, J., Deneux, F., Belsher, T., Sauzade, D., Boudouresque, C.F., Charbonnel,
497 E., Emery, E., Herve, G., Bonhomme, P., 2001. Etude et cartographie des biocénoses de
498 la rade de Toulon, in: Contrat D'étude Pour Le Syndicat Intercommunal de l'Aire
499 Toulonnaise, Ifremer et GISPosidonie. Ifremer Publ, La Seyne, p. 150.

500 Bigeleisen, J., 1996. Nuclear size and shape effects in chemical reactions. Isotope chemistry
501 of the heavy elements. *J. Am. Chem. Soc.* 118, 3676–3680. doi:10.1021/ja954076k

502 Brennecka, G., Wasylenki, L.E., Weyer, S., Anbar, a D., 2011. Uranium isotope fractionation
503 during adsorption to manganese oxides. *Environ. Sciene Technol.* 1370–1375.

504 Chaillou, G., Anschutz, P., Lavaux, G., Schäfer, J., Blanc, G., 2002. The distribution of Mo,
505 U, and Cd in relation to major redox species in muddy sediments of the Bay of Biscay.
506 *Mar. Chem.* 80, 41–59. doi:10.1016/S0304-4203(02)00097-X

507 Chen, J.H., Lawrence Edwards, R., Wasserburg, G.J., 1986. ^{238}U , ^{234}U and ^{232}Th in
508 seawater. *Earth Planet. Sci. Lett.* 80, 241–251. doi:10.1016/0012-821X(86)90108-1

509 Collier, R.W., 1985. Molybdenum in the Northeast Pacific Ocean. *Limnol. Oceanogr.* 30,
510 1351–1354. doi:10.4319/lo.1985.30.6.1351

511 Dang, D.H., Breda, N., Wang, W., Georg, R.B., Evans, D., 2016. Uranium isotope
512 fractionation during adsorption, (co)precipitation and biotic reduction. *Environ. Sci.*
513 *Technol.* 50, 12695–12704.

514 Dang, D.H., Lenoble, V., Durrieu, G., Mullot, J.-U., Mounier, S., Garnier, C., 2014a.
515 Sedimentary dynamics of coastal organic matter: An assessment of the porewater
516 size/reactivity model by spectroscopic techniques. *Estuar. Coast. Shelf Sci.* 151, 100–

517 111. doi:10.1016/j.ecss.2014.10.002

518 Dang, D.H., Lenoble, V., Durrieu, G., Omanović, D., Mullot, J.-U., Mounier, S., Garnier, C.,
519 2015a. Seasonal variations of coastal sedimentary trace metals cycling: Insight on the
520 effect of manganese and iron (oxy)hydroxides, sulphide and organic matter. *Mar. Pollut.*
521 *Bull.* 92, 113–124. doi:10.1016/j.marpolbul.2014.12.048

522 Dang, D.H., Schaefer, J., Brach-Papa, C., Lenoble, V., Durrieu, G., Dutruch, L., Chiffolleau,
523 J.-F., Gonzalez, J.-L., Blanc, G., Mullot, J.U., Mounier, S., Garnier, C., 2015b.
524 Evidencing the impact of coastal contaminated sediments on mussels through Pb stable
525 isotopes composition. *Environ. Sci. Technol.* 49, 11438–11448.
526 doi:10.1021/acs.est.5b01893

527 Dang, D.H., Tessier, E., Lenoble, V., Durrieu, G., Omanović, D., Mullot, J.-U., Pfeifer, H.-R.,
528 Mounier, S., Garnier, C., 2014b. Key parameters controlling arsenic dynamics in coastal
529 sediments: an analytical and modeling approach. *Mar. Chem.* 161, 34–46.

530 Dufresne, C., Duffa, C., Rey, V., 2014. Wind-forced circulation model and water exchanges
531 through the channel in the Bay of Toulon. *Ocean Dyn.* 64, 209–224.
532 doi:10.1007/s10236-013-0676-3

533 Fujii, Y., Higuchi, N., Haruno, Y., Nomura, M., Suzuki, T., 2006. Temperature dependence of
534 isotope effects in uranium chemical exchange reactions. *J. Nucl. Sci. Technol.* 43, 400–
535 406. doi:10.1080/18811248.2006.9711111

536 Ginder-Vogel, M., Stewart, B., Fendorf, S., 2010. Kinetic and mechanistic constraints on the
537 oxidation of biogenic uraninite by ferrihydrite. *Environ. Sci. Technol.* 44, 163–169.
538 doi:10.1021/es902452u

539 Goldmann, A., Brenneka, G., Noordmann, J., Weyer, S., Wadhwa, M., 2015. The uranium
540 isotopic composition of the Earth and the Solar System. *Geochim. Cosmochim. Acta*
541 148, 145–158. doi:10.1016/j.gca.2014.09.008

542 Goto, K.T., Anbar, A.D., Gordon, G.W., Romaniello, S.J., Shimoda, G., Takaya, Y.,
543 Tokumaru, A., Nozaki, T., Suzuki, K., Machida, S., Hanyu, T., Usui, A., 2014. Uranium
544 isotope systematics of ferromanganese crusts in the Pacific Ocean: Implications for the
545 marine $^{238}\text{U}/^{235}\text{U}$ isotope system. *Geochim. Cosmochim. Acta* 146, 43–58.

doi:10.1016/j.gca.2014.10.003

Helz, G.R., Miller, C. V., Charnock, J.M., Mosselmans, J.F.W., Pattick, R. a D., Garner, C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochim. Cosmochim. Acta* 60, 3631–3642. doi:10.1016/0016-7037(96)00195-0

Holmden, C., Amini, M., Francois, R., 2015. Uranium isotope fractionation in Saanich Inlet: A modern analog study of a paleoredox tracer. *Geochim. Cosmochim. Acta* 153, 202–215. doi:10.1016/j.gca.2014.11.012

IRMM, 2015. Nuclear certified reference materials, Institute for Reference Materials and Measurements (IRMM). Geel, Belgium.

Kyte, F.T., Leinen, M., Ross Heath, G., Zhou, L., 1993. Cenozoic sedimentation history of the central North Pacific: Inferences from the elemental geochemistry of core LL44-GPC3. *Geochim. Cosmochim. Acta* 57, 1719–1740. doi:10.1016/0016-7037(93)90109-A

Laliche, K., Venier, R., Degoutte, G., Meriaux, P., Patouillet, B., Bailleul, J., Laliche, K., Venier, R., Degoutte, G., Meriaux, P., Patouillet, B., 2015. Dardennes dam: foundation investigations and diagnosis before reinforcement studies, in: Colloque CFBR ” Fondations Des Barrages : Caracterisation, Traitements, Surveillance, Rehabilitation ”.

Lyons, T.W., Reinhard, C.T., Planavsky, N.J., 2014. The rise of oxygen in Earth’s early ocean and atmosphere. *Nature* 506, 307–15. doi:10.1038/nature13068

McManus, J., Berelson, W.M., Klinkhammer, G.P., Hammond, D.E., Holm, C., 2005. Authigenic uranium: Relationship to oxygen penetration depth and organic carbon rain. *Geochim. Cosmochim. Acta* 69, 95–108. doi:10.1016/j.gca.2004.06.023

McManus, J., Berelson, W.M., Severmann, S., Poulson, R.L., Hammond, D.E., Klinkhammer, G.P., Holm, C., 2006. Molybdenum and uranium geochemistry in continental margin sediments: Paleoproxy potential. *Geochim. Cosmochim. Acta* 70, 4643–4662. doi:10.1016/j.gca.2006.06.1564

Montoya-Pino, C., Weyer, S., Anbar, A.D., Pross, J., Oschmann, W., van de Schootbrugge, B., Arz, H.W., 2010. Global enhancement of ocean anoxia during oceanic anoxic event 2: A quantitative approach using U isotopes. *Geology* 38, 315–318.

575 doi:10.1130/G30652.1

576 Morford, J.L., Emerson, S.R., Breckel, E.J., Kim, S.H., 2005. Diagenesis of oxyanions (V, U,
577 Re, and Mo) in pore waters and sediments from a continental margin. *Geochim.*
578 *Cosmochim. Acta* 69, 5021–5032. doi:10.1016/j.gca.2005.05.015

579 Morford, J.L., Martin, W.R., François, R., Carney, C.M., 2009. A model for uranium,
580 rhenium, and molybdenum diagenesis in marine sediments based on results from coastal
581 locations. *Geochim. Cosmochim. Acta* 73, 2938–2960. doi:10.1016/j.gca.2009.02.029

582 Noordmann, J., Weyer, S., Montoya-Pino, C., Dellwig, O., Neubert, N., Eckert, S., Paetzel,
583 M., Böttcher, M.E., 2015. Uranium and molybdenum isotope systematics in modern
584 euxinic basins: Case studies from the central Baltic Sea and the Kyllaren fjord (Norway).
585 *Chem. Geol.* 396, 182–195. doi:10.1016/j.chemgeo.2014.12.012

586 Région Provence Alpes Côte d’Azur, 2008. Le Las : Une Rivière dans la Ville. Val d’As,
587 Toulon.

588 Romaniello, S.J., Herrmann, A.D., Anbar, A.D., 2013. Uranium concentrations and
589 $^{238}\text{U}/^{235}\text{U}$ isotope ratios in modern carbonates from the Bahamas: Assessing a novel
590 paleoredox proxy. *Chem. Geol.* 362, 305–316. doi:10.1016/j.chemgeo.2013.10.002

591 Salome, K.R., Green, S.J., Beazley, M.J., Webb, S.M., Kostka, J.E., Taillefert, M., 2013. The
592 role of anaerobic respiration in the immobilization of uranium through biomineralization
593 of phosphate minerals. *Geochim. Cosmochim. Acta* 106, 344–363.
594 doi:10.1016/j.gca.2012.12.037

595 Siebert, C., Nägler, T.F., von Blanckenburg, F., Kramers, J.D., 2003. Molybdenum isotope
596 records as a potential new proxy for paleoceanography. *Earth Planet. Sci. Lett.* 211, 159–
597 171. doi:10.1016/S0012-821X(03)00189-4

598 Stewart, B.D., Girardot, C., Spycher, N., Sani, R.K., Peyton, B.M., 2012. Influence of
599 chelating agents on biogenic uraninite reoxidation by Fe(III) (hydr)oxides. *Environ. Sci.*
600 *Technol.* 47, 364–371. doi:10.1021/es303022p

601 Stirling, C.H., Andersen, M.B., Potter, E.K., Halliday, A.N., 2007. Low-temperature isotopic
602 fractionation of uranium. *Earth Planet. Sci. Lett.* 264, 208–225.
603 doi:10.1016/j.epsl.2007.09.019

604 Stirling, C.H., Andersen, M.B., Warthmann, R., Halliday, A.N., 2015. Isotope fractionation of
605 ^{238}U and ^{235}U during biologically-mediated uranium reduction. *Geochim. Cosmochim.*
606 *Acta* 163, 200–218. doi:10.1016/j.gca.2015.03.017

607 Stylo, M., Neubert, N., Wang, Y., Monga, N., Romaniello, S.J., Weyer, S., Bernier-Latmani,
608 R., 2015. Uranium isotopes fingerprint biotic reduction. *Proc. Natl. Acad. Sci. U. S. A.*
609 112, 5619–24. doi:10.1073/pnas.1421841112

610 Sundby, B., Martinez, P., Gobeil, C., 2004. Comparative geochemistry of cadmium, rhenium,
611 uranium, and molybdenum in continental margin sediments. *Geochim. Cosmochim. Acta*
612 68, 2485–2493. doi:10.1016/j.gca.2003.08.011

613 Tessier, E., Garnier, C., Mullet, J.-U., Lenoble, V., Arnaud, M., Raynaud, M., Mounier, S.,
614 2011. Study of the spatial and historical distribution of sediment inorganic contamination
615 in the Toulon bay (France). *Mar. Pollut. Bull.* 62, 2075–2086.
616 doi:10.1016/j.marpolbul.2011.07.022

617 Tissot, F.L.H., Dauphas, N., 2015. Uranium isotopic compositions of the crust and ocean:
618 Age corrections, U budget and global extent of modern anoxia. *Geochim. Cosmochim.*
619 *Acta* 167, 113–143. doi:10.1016/j.gca.2015.06.034

620 Tribouillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and
621 paleoproductivity proxies: An update. *Chem. Geol.* 232, 12–32.
622 doi:10.1016/j.chemgeo.2006.02.012

623 Turekian, K.K., Wedepohl, K.H., 1961. Geological Society of America Bulletin Distribution
624 of the Elements in Some Major Units of the Earth's Crust. *Geol. Soc. Am. Bull.* 72,
625 175–192. doi:10.1130/0016-7606(1961)72

626 Weber, K.A., Cameron Thrash, J., Ian Van Trump, J., Achenbach, L.A., Coates, J.D., 2011.
627 Environmental and taxonomic bacterial diversity of anaerobic uranium(IV) bio-
628 oxidation. *Appl. Environ. Microbiol.* 77, 4693–4696. doi:10.1128/AEM.02539-10

629 Weyer, S., Anbar, a. D., Gerdes, a., Gordon, G.W., Algeo, T.J., Boyle, E. a., 2008. Natural
630 fractionation of $^{238}\text{U}/^{235}\text{U}$. *Geochim. Cosmochim. Acta* 72, 345–359.
631 doi:10.1016/j.gca.2007.11.012

632 Yamada, M., Wang, Z.-L., Kato, Y., 2006. Precipitation of authigenic uranium in suboxic

633 continental margin sediments from the Okinawa Trough. *Estuar. Coast. Shelf Sci.* 66,
634 570–579. doi:10.1016/j.ecss.2005.11.002

635 Zheng, Y., Anderson, R.F., Van Geen, A., Kuwabara, J., 2000. Authigenic molybdenum
636 formation in marine sediments: A link to pore water sulfide in the Santa Barbara Basin.
637 *Geochim. Cosmochim. Acta* 64, 4165–4178. doi:10.1016/S0016-7037(00)00495-6
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 2

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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 ± 0.05					0.21 ± 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 ± 1.9					58.8 ± 7.7				
Ti/Al x 100 (±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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