

1  **$^{238}\text{U}/^{235}\text{U}$  in calcite is more susceptible to carbonate diagenesis**

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## 12 Abstract

13 The uranium isotopic composition ( $\delta^{238}\text{U}$ ) of bulk marine calcium carbonates has been  
14 extensively explored as a promising paleoredox proxy to track the extent of global oceanic anoxia  
15 in deep time. Multiple studies have examined whether primary calcium carbonates can directly  
16 capture seawater  $\delta^{238}\text{U}$  and whether bulk measurements of recent and ancient carbonates preserve  
17 seawater U isotope signatures. Here we assess the role of diagenesis in altering  $\delta^{238}\text{U}$  signatures  
18 in carbonates sediments that have a primary calcitic mineralogy at the Paleocene-Eocene Thermal  
19 Maximum (PETM), an interval with rapid global warming and oceanic deoxygenation at ~56  
20 million years ago.

21 Although primary abiotic and biogenic calcium carbonates (aragonite and calcite) can  
22 directly capture seawater  $\delta^{238}\text{U}$  with small offsets ( $< 0.1\text{‰}$ ) relative to modern seawater, diagenetic  
23 alteration of Bahamian shallow-water platform carbonate sediments that have a predominantly  
24 primary aragonitic mineralogy resulted in significantly larger offsets (up to  $0.6\text{‰}$ ). Since U  
25 concentration in aragonite is at least one order of magnitude higher than calcite ( $> 1$  ppm vs.  $< 0.1$   
26 ppm),  $\delta^{238}\text{U}$  in calcite should be even more susceptible to diagenesis than that in aragonite.

27 We find strong evidence of this effect in analysis of  $\delta^{238}\text{U}$  in PETM shallow-water  
28 carbonate sediments from Drilling Project (ODP) Hole 871C (Limalok Guyot, Pacific Ocean). Our  
29 results reveal large fluctuations in bulk carbonate  $\delta^{238}\text{U}$  from  $-0.69$  to  $+0.71\text{‰}$  around the PETM  
30 boundary but consistently heavier  $\delta^{238}\text{U}$  (between  $-0.14$  and  $+0.47\text{‰}$ ) than modern seawater  
31 outside of this interval. The significantly lighter  $\delta^{238}\text{U}$  values than modern seawater were  
32 interpreted to result from the operation of a Mn oxide shuttle. The heavier  $\delta^{238}\text{U}$  values are most  
33 likely caused by authigenic reductive accumulation of U(IV) in pore waters below the sediment-  
34 water interface. We found that carbonate  $\delta^{238}\text{U}$  values higher than modern seawater tend to

35 increase with increasing U/Ca. This relationship is well-explained by an authigenic reductive  
36 accumulation model that simply assumes addition to primary calcite during diagenesis of calcitic  
37 cements containing isotopically heavier U(IV).

38 Our work confirms expectations that  $\delta^{238}\text{U}$  in primary calcite is more susceptible to the  
39 amount of diagenetic cementation compared to primary aragonite, and that variations of  $\delta^{238}\text{U}$  in  
40 carbonate sediments with a primary calcitic mineralogy would more dominantly reflect the local  
41 redox state of depositional and early diagenetic environments. It is essential to identify the original  
42 carbonate mineralogy, the diagenetic history, and constrain the redox state of local deposition  
43 environments of sedimentary carbonate rocks when applying bulk carbonate  $\delta^{238}\text{U}$  as a global  
44 proxy for oceanic anoxia in deep time.

45

46 **Keywords:** U isotopes; calcite and aragonite; paleoredox proxy; diagenesis; local and global

## 47 1. Introduction

48           Reconstructing Earth's oxygenation history is key to our understanding of the evolution of  
49 life because the rise and fall of atmospheric oxygen through time strongly affects, and is affected  
50 by, the biosphere (e.g., Fenchel and Finlay, 1994; Berner et al., 2007; Lyons et al., 2014). For  
51 example, the emergence and evolution of early animal life in the Late-Neoproterozoic was  
52 associated with the oxygenation of the atmosphere and oceans, whereas the three major mass  
53 extinction events of the Phanerozoic—in the Late Devonian, end-Permian, and end-Triassic—  
54 coincided with oceanic anoxia (e.g., Canfield et al., 2007; Berner et al., 2007; Mills et al., 2014;  
55 Reinhard et al., 2016). These intimate links indicate that it is crucial to reconstruct Earth's  
56 oxygenation history to unravel the co-evolution of life and Earth.

57           Multiple geochemical proxies can be used to reconstruct Earth's oxygenation history from  
58 a wide range of sedimentary rock types, including the abundance of redox-sensitive elements (e.g.,  
59 V, Mo, Re, U, Cr, I/Ca), and the stable isotopic composition of light elements ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{34}\text{S}$ )  
60 and heavy elements ( $\delta^{56}\text{Fe}$ ,  $\delta^{53}\text{Cr}$ ,  $\delta^{51}\text{V}$ ,  $\delta^{82}\text{Se}$ ,  $\delta^{98}\text{Mo}$ ,  $\epsilon^{205}\text{Tl}$ ,  $\delta^{238}\text{U}$ ) (e.g., Anbar and Rouxel,  
61 2007; Lyons et al., 2009; Pufahl and Hiatt, 2012; Fan et al., 2021; Lu et al., 2010). Among these  
62 paleoredox proxies, variations of  $\delta^{238}\text{U}$  in sedimentary carbonate rocks are being explored as a  
63 novel tool to track the global redox conditions of oceans through time (e.g., Brennecka et al.,  
64 2011a; Lau et al., 2016; del Rey et al., 2020; Clarkson et al., 2021; Song et al., 2017; White et al.,  
65 2018; Elrick et al., 2017; Cheng et al., 2020; Wei et al., 2018; Zhang et al., 2018; Gilleaudeau et  
66 al., 2019; Tostevin et al., 2019). Uranium isotopic mass balance in modern oceans demonstrates  
67 that seawater  $\delta^{238}\text{U}$  is driven by variations in ocean redox conditions (Andersen et al., 2017; Weyer  
68 et al., 2008). Uranium in the oceans mainly comes from continental weathering, with negligible  
69 isotope fractionation (Andersen et al., 2015, 2017; Tissot and Dauphas, 2015; Weyer et al., 2008).

70 Marine U is mainly removed by reduction of dissolved U(VI) as insoluble U(IV), adsorption to Fe  
71 and Mn oxides (e.g., ferromanganese crust and nodules), coprecipitation with calcium carbonates,  
72 and hydrothermal alteration (Dunk et al., 2002). Among these U removal processes, U reduction  
73 is the most efficient pathway and causes the largest isotope fractionation  $\sim 1\%$  (Andersen et al.,  
74 2015, 2017; Tissot and Dauphas, 2015; Weyer et al., 2008). Hence, seawater  $\delta^{238}\text{U}$  is  
75 predominantly driven by the redox conditions of the oceans. Since U has a relatively long residence  
76 time ( $\sim 500$  kyr), compared to the ocean mixing time ( $\sim 2$  kyr, Dunk et al., 2002; Ku et al., 1977),  
77  $\delta^{238}\text{U}$  at any location of the open oceans should be homogeneous, reflecting the average global  
78 redox state. If U isotopes in marine calcium carbonates capture and preserve the coeval seawater  
79 U isotopic composition, then  $\delta^{238}\text{U}$  in carbonate rocks can be used to reconstruct the global redox  
80 conditions of ancient oceans. The robustness of this paleoredox proxy relies heavily on this  
81 assumption.

82 Multiple studies have explored the reliability of this proxy by examining two questions:  
83 (1) whether primary abiotic and biogenic calcium carbonates can directly capture coeval seawater  
84 U isotopic composition, and (2) whether bulk carbonate sediments can preserve the original  $\delta^{238}\text{U}$   
85 in primary calcium carbonates during diagenesis. Laboratory experiments and field work revealed  
86 small or negligible isotope fractionations ( $< 0.10\%$ ) in primary calcium carbonates (Chen et al.,  
87 2016, 2018a; Livermore et al., 2020), answering the first question. Calcium carbonate  
88 coprecipitation experiments demonstrated a small isotope fractionation of  $\sim 0.10\%$  during U(VI)  
89 incorporation into abiotic aragonite but not calcite under pH  $\sim 8.5$  (Chen et al., 2016). Field work  
90 also revealed that biological effects can cause variable U isotope fractionation ( $0 - 0.09\%$ ) during  
91 U uptake by primary biogenic calcium carbonates such as ooids, stromatolites, corals, red and  
92 green calcareous algae, microbial calcite, and brachiopods (Chen et al., 2018a, 2021; Romaniello

93 et al., 2013; Weyer et al., 2008; Stirling et al., 2007; Andersen et al., 2016; Tissot and Dauphas,  
94 2015; Livermore et al., 2020). Briefly, precipitation of primary abiotic and biogenic calcium  
95 carbonates can directly capture seawater  $\delta^{238}\text{U}$  with small or little isotopic offsets of less than  
96 0.10‰.

97 In contrast, diagenesis has been demonstrated to significantly impact, to varying degrees,  
98  $\delta^{238}\text{U}$  in bulk carbonate sediments compared to  $\delta^{238}\text{U}$  of primary calcium carbonates. Modern  
99 carbonate sediments deposited under anoxic bottom waters record significant U isotopic offsets  
100 from water column values. Recent work revealed a U isotopic offset of  $\sim+0.6\text{‰}$  (relative to bottom  
101 waters) in carbonate sediments derived from microbial calcite that were deposited beneath sulfidic  
102 bottom waters, in the modern redox-stratified lake Fayetteville Green Lake (New York, USA)  
103 (Chen et al., 2021). This finding reflects the typical U isotope fractionation observed in other  
104 modern organic-rich sediments deposited under anoxic bottom waters (Andersen et al., 2014,  
105 2017). Anoxic deposition was also suggested to cause isotopic offsets of 0.4 – 0.6‰ (relative to  
106 coeval seawater) in Paleocene-Eocene deep-sea pelagic carbonates that were originally  
107 foraminiferal calcite (Clarkson et al., 2021). Anoxic depositional environments typically result in  
108 reduction of dissolved U(VI) in anoxic water columns and pore waters below the sediment-water  
109 interface, leading to significant sedimentary authigenic enrichments of isotopically heavier U(IV)  
110 ( $> 10$  ppm, e.g., Partin et al., 2013). Since U in primary biogenic calcite is typically low (0.2 – 30  
111 ppb; e.g., Russell et al., 2004; Chen et al., 2018a, 2020; Keul et al., 2013; Allen et al., 2016), the  
112 anoxic deposition of authigenic carbonate sediments can easily overprint the original  $\delta^{238}\text{U}$  in  
113 primary calcite grains.

114 Modern Bahamian shallow-water platform carbonate sediments (predominantly aragonitic  
115 mineralogy) deposited under oxic bottom waters with reducing pore waters also record carbonate

116  $\delta^{238}\text{U}$  values higher than modern seawater ( $-0.14 \pm 0.15\text{‰}$ ,  $N = 162$ ,  $1\sigma$ , vs. seawater =  $-0.392 \pm$   
117  $0.005\text{‰}$ ) (Romaniello et al., 2013; Chen et al., 2018b, 2020; Tissot and Dauphas, 2015; Tissot et  
118 al., 2018; Russell et al, 2004). The positive isotope offsets in these carbonate sediments were  
119 interpreted to result from authigenic reductive accumulation of U(IV), by a concentration of  $\sim 2.5$   
120  $\pm 1$  ppm, below the sediment-water interface. The concentration of U(IV) in these shallow-water  
121 carbonates, derived authigenically during diagenesis, is at least two orders of magnitude higher  
122 than the U concentration in primary calcite precipitates (0.2 – 30 ppb, e.g., Russell et al., 2004;  
123 Chen et al., 2018a, 2020; Keul et al., 2013; Allen et al., 2016), suggesting that  $\delta^{238}\text{U}$  in carbonate  
124 sediments with a primary calcitic mineralogy should be more easily offset from seawater  $\delta^{238}\text{U}$ ,  
125 compared to carbonate sediments with a primary aragonitic mineralogy which typically have  
126 significantly higher U concentrations at least one order of magnitude of higher than calcite (e.g.,  
127 Reeder et al., 2000; Keul et al., 2013; Romaniello et al., 2013).

128 To explore the potential effects of diagenesis on shallow-water carbonate sediments  
129 deposited beneath oxic bottom waters with a primary calcitic mineralogy, we collected samples  
130 from a Paleogene carbonate platform succession recovered from Limalok Guyot (Pacific Ocean)  
131 at Ocean Drilling Project (ODP) Site 871. Bulk carbonate samples were measured for trace element  
132 and rare earth element concentrations and  $\delta^{238}\text{U}$  values. Our results documented positive U-  
133 isotopic offsets ( $\sim 0.5 - 1.2\text{‰}$  relative to coeval seawater) that increased with U/Ca and negative  
134 isotopic offsets ( $\sim 0.2\text{‰}$ ) that might be associated with a Mn oxide shuttle.

135

## 136 **2. Samples**

137 Our geochemical data are derived from ODP Site 871 on Limalok Guyot in the Pacific  
138 Ocean, drilled during ODP Leg 144 (Premoli-Silva et al., 1993). At Hole 871C,  $\sim 300$  m of a

139 Paleogene carbonate platform (from 133.7 to 422.9 meters below seafloor (mbsf)) overlying a  
140 volcanic edifice was cored (Premoli Silva et al., 1993; Watkins et al., 1995; Wilson et al., 1998).  
141 Carbonates from Hole 871C primarily consist of benthic foraminiferal packstone/wackestone,  
142 miliolid-intraclast grainstone, and rohodolith grain/packstone, which have a predominantly  
143 primary calcitic mineralogy (Premoli Silva et al., 1993; Ogg et al., 1995; Scholle and Ulmer-  
144 Scholle, 2003). Shipboard analyses indicate that the shallow-water carbonates from Hole 871C  
145 have calcium carbonate contents of 95 – 98% and contain less than 0.3% organic carbon and no  
146 sulfur (Premoli Silva et al., 1993).

147         Previous work on the shallow-water carbonate sediments from Hole 871C has explored the  
148 diagenetic and stratigraphic history in some detail. On the basis of petrography and stable-isotopic  
149 geochemistry, Wyatt et al. (1995) concluded that most of the diagenetic alteration and cementation  
150 occurred in the marine realm, largely during early marine diagenesis (rather than meteoric or burial  
151 diagenesis). The existence of some limited intervals with well-developed moldic and vuggy  
152 porosity and light oxygen isotope values was taken to indicate some possible meteoric diagenesis,  
153 although classic indicators (such as vadose-zone cements and depleted  $\delta^{13}\text{C}_{\text{carb}}$  values) have not  
154 been reported. Robinson (2011) used high-resolution stable-isotope measurements and  
155 biostratigraphy to argue for the existence of a partial record of the Paleocene-Eocene Thermal  
156 Maximum (PETM) in Hole 871C.

157         Twenty-nine samples from Hole 871C were selected for  $\delta^{238}\text{U}$  characterization, from 150  
158 to 420 mbsf which covers the approximate time interval 46 – 58 Ma (based on the age model of  
159 Robinson, 2011). We sampled carbonates at high-resolution over the Paleocene-Eocene Thermal  
160 Maximum (PETM) interval (335.80 – 336.30 mbsf) and earliest Eocene (321.21 – 326.42 mbsf)



161 to see if we could capture any variations in seawater  $\delta^{238}\text{U}$  related to global oceanic deoxygenation  
162 during that event that were preserved despite diagenesis.

163

### 164 **3. Methods**

#### 165 **3.1 Trace metal and rare earth elements concentration analysis**

166 For each sample, about two grams of carbonate were powdered and homogenized using a  
167 ball mill equipped with silicon carbide mortars. Then, approximately 0.5 – 1 g powdered carbonate  
168 sediments from each sample were leached with 1 M trace-metal grade nitric acid overnight to  
169 extract the fraction of U associated with carbonates. The resulting solutions were then centrifuged  
170 at 4500 rpm for 30 min to remove insoluble solids. A small aliquot of the supernatant was diluted  
171 in 2% nitric acid for the measurement of trace element and rare earth element (REE) concentrations  
172 on a Thermo iCAP Q inductively coupled plasma mass spectrometer (ICP-MS) at W. M. Keck  
173 Foundation Laboratory for Environmental Biogeochemistry, Arizona State University. The cerium  
174 anomaly ( $\text{Ce}/\text{Ce}^*$ ) is calculated based on its geometric average relative to its neighbor elements Pr  
175 and Nd (e.g., Ling et al., 2011; Tostevin et al., 2016) and normalized to the average Post-Archean  
176 Australian shale (PAAS) using the equation:

$$\text{Ce}/\text{Ce}^* = \text{Ce} \times \text{Pr}/\text{Nd}^2 \quad (1)$$

#### 177 **3.2 Uranium isotope analysis**

178 Based on the measured trace element concentration data, approximately 250 ng U was  
179 taken from each sample and spiked with a  $^{233}\text{U}$ - $^{236}\text{U}$  double-spike (IRMM-3636) at a  $U_{\text{spike}}:U_{\text{sample}}$   
180 ratio of 0.0363 (Verbruggen et al., 2008). These sample solutions were digested with aqua regia  
181 and conc.  $\text{HNO}_3 + 30\% \text{H}_2\text{O}_2$  to removal organic matter. The digested samples were dissolved in  
182 3 M  $\text{HNO}_3$  for purification of U by chromatographic column chemistry.

183 Purification of U followed the Eichrom UTEVA resin procedure (Chen et al., 2016a;  
184 Weyer et al., 2008). Briefly, ~ 1 ml UTEVA resin (Eichrom Technologies, LLC) was loaded into  
185 10 ml chromatography columns (Bio-Rad Laboratories, Inc.), and rinsed with 2.5 ml 0.05 M HCl  
186 four times to remove any U induced during the loading step. Then, the resin was conditioned with  
187  $3 \times 1$  ml 3 M HNO<sub>3</sub>. Samples (dissolved in 3 M HNO<sub>3</sub>) were load onto the columns and washed  
188 with 15 ml 3 M HNO<sub>3</sub> to clean all the matrix ions except U and Th. Following this, the resin was  
189 rinsed with 10 M HCl ( $3 \times 1$  ml) to convert it to chloride form. Th on the resin was then removed  
190 using 5 M HCl + 0.05 M oxalic acid ( $3 \times 0.8$  ml). The oxalic acid left on the resin was cleaned  
191 using 5 M HCl ( $3 \times 1$  ml). Finally, U adsorbed to the UTEVA was eluted using 0.05 M HCl (~7  
192 ml). The eluted U cuts were dried down and digested with conc. HNO<sub>3</sub> + 30% H<sub>2</sub>O<sub>2</sub> to get rid of  
193 organic residue eluted from the UTEVA resin.

194 After purification, U isotopic ratios were measured at a U concentration of ~50 ppb in 2%  
195 trace metal clean nitric acid on a Thermo Scientific Neptune MC-ICP-MS equipped with an ESI  
196 Apex desolvating nebulizer at ASU (W. M. Keck Foundation Laboratory for Environmental  
197 Biogeochemistry, Arizona State University). Ion beams of <sup>233</sup>U, <sup>235</sup>U, <sup>236</sup>U and <sup>238</sup>U were collected  
198 with Faraday cups connected to 10<sup>11</sup> Ω, 10<sup>11</sup> Ω, 10<sup>11</sup> Ω, 10<sup>10</sup> Ω resistors. The signal for <sup>238</sup>U from  
199 a 50 ppb U solution was ~ 30 volts. Uranium isotopic composition was reported in δ notation in  
200 per mil (‰) relative to the U reference standard CRM-145a:

$$\delta^{238\text{U}} = \left[ \frac{\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{sample}}}{\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{CRM-145a}}} - 1 \right] \times 1000 \quad (2)$$

201 At least three replicate measurements were performed for each sample. The uncertainty in  
202  $\delta^{238\text{U}}$  was reported as twice the standard deviation of either the sample or the standard CRM-145a.

203 The blank for the U column chemistry was  $< 0.05$  ng. The reproducibility of the repeated  
204 measurements of  $\delta^{238}\text{U}$  in CRM-145a was  $\pm 0.08\text{‰}$  (2 SD, N = 45). The accuracy of U isotope  
205 analysis was monitored by analyzing the secondary standard CRM-129a. The average  $\delta^{238}\text{U}$  value  
206 for this standard was  $-1.79 \pm 0.08\text{‰}$  (2 SD, N = 25), in good agreement with previous published  
207 data ( $-1.70 \pm 0.08\text{‰}$  and  $-1.72 \pm 0.10\text{‰}$  (2 SD); Chen et al., 2018b; Wang et al., 2015).

208

## 209 **4. Results**

### 210 **4.1 Concentration of redox-sensitive elements and Ce anomaly**

211 The shallow-water carbonates in Hole 871C documented different extents of enrichments  
212 of redox-sensitive elements (“RSE”) V, Mo, Re, and U (Fig. 2A – D; see Table S1 in  
213 Supplementary information). The leached carbonate fraction from each sample contained an  
214 undetectable amount of Al and Th (see Table S1 in Supplementary information). As a result, we  
215 infer that the concentrations of RSE measured in our acid-leached samples include negligible  
216 contributions from detrital materials. Vanadium concentration varied between 1 and 30 ppm,  
217 increased to up to 70 ppm over the PETM interval (317 – 336 mbsf defined by Robinson, 2011),  
218 and decreased back to  $< 30$  ppm above 336 mbsf. Both Mo ( $< 0.1$  ppm) and Re ( $< 3$  ppb)  
219 concentrations remained relatively low and invariant beyond the PETM interval with occasionally  
220 one and two data points of high concentrations of Mo ( $\sim 2$  ppm) and Re (4 and 7 ppb). Uranium  
221 concentration below the boundary varied between 0.2 and 5 ppm, elevated up to 18 ppm over the  
222 interval, and immediately decreased back to  $< 4$  ppm. The cerium anomaly ( $\text{Ce}/\text{Ce}^*$ ) was  
223 consistently  $< 0.5$  throughout the whole carbonate section (see the rare earth elements (REEs) data  
224 and full REE pattern in Table S1 and Figure S1, respectively, in the supplementary material).

225

## 226 4.2 Bulk carbonate $\delta^{238}\text{U}$ from ODP Hole 871C

227 Bulk shallow-water carbonate  $\delta^{238}\text{U}$  from ODP Hole 871C is generally heavier than the  
228 reported Paleocene-Eocene seawater ( $-0.36\text{‰}$ ; Clarkson et al., 2021) varying between  $-0.14$  and  
229  $0.47\text{‰}$ , except during the PETM interval and lowermost Eocene, from which bulk carbonate  $\delta^{238}\text{U}$   
230 fluctuate significantly between  $-0.69$  to  $+0.71\text{‰}$  (Fig. 3D; see Table 1). In detail,  $\delta^{238}\text{U}$  values  
231 decrease continuously from  $+0.71$  to  $-0.53\text{‰}$  between 336.30 and 335.80 mbsf (Fig. 3E) while  
232 they increase progressively from  $-0.73$  to  $-0.46\text{‰}$  between 326.42 to 326.26 mbsf except for one  
233 data point with a positive value of  $0.46\text{‰}$  (Fig. 3E).

234

## 235 5. Discussion

236 Our data document  $\delta^{238}\text{U}$  values lighter than modern seawater over the PETM to lower  
237 Eocene interval, and consistently higher  $\delta^{238}\text{U}$  values ( $> -0.39\text{‰}$ ) beyond this interval. To interpret  
238 these U isotope data, we first constrain the seawater  $\delta^{238}\text{U}$  over the Paleocene-Eocene and the  
239 redox state of local depositional environments. Then, we explore the possible mechanisms that  
240 cause the lighter and higher  $\delta^{238}\text{U}$  values in ODP Hole 871C. Finally, we discuss the implications  
241 of bulk carbonate  $\delta^{238}\text{U}$  as a paleoredox proxy to infer global redox conditions of oceans in deep  
242 time.

243

### 244 5.1 Seawater $\delta^{238}\text{U}$ over the Paleocene-Eocene

245 To explore the effects of diagenesis on U isotopes in Paleocene-Eocene carbonate  
246 sediments, it is essential to constrain coeval seawater  $\delta^{238}\text{U}$ , which is predominantly controlled by  
247 the global redox state of the oceans. Measurements of U isotopes in ferromanganese crusts  
248 revealed an invariant isotopic offset of  $-0.24\text{‰}$  from modern seawater, suggesting that seawater

249  $\delta^{238}\text{U}$  did not change over the Cenozoic (Wang et al., 2016). High-resolution profiles of pelagic  
250 carbonate  $\delta^{238}\text{U}$  data over the PETM suggested a limited expansion of oceanic anoxia and that  
251 Paleocene-Eocene seawater had a  $\delta^{238}\text{U}$  value of  $-0.36\text{‰}$  (Clarkson et al., 2021), very close to  
252 modern seawater  $\delta^{238}\text{U}$  ( $-0.392 \pm 0.005\text{‰}$ ; Tissot et al., 2015). The limited expansion of oceanic  
253 anoxia is supported by a cGENIE model result that suggests anoxia/dysoxia rose by 2% to reach  
254 4% of the global ocean volume during the transition from pre-PETM to PETM (Remmelzwaal et  
255 al., 2019). For simplicity, we assume that Paleocene-Eocene seawater  $\delta^{238}\text{U}$  remained invariant  
256 around  $-0.39\text{‰}$ .

257

## 258 **5.2 Redox state of local depositional environments for ODP Hole 871C**

259 Previous studies revealed that the redox state of local depositional environments  
260 significantly affects  $\delta^{238}\text{U}$  measured in bulk carbonate sediments. Specifically, carbonate  
261 sediments deposited under reducing bottom waters exhibited profound enrichments in U  
262 concentration, and consistently higher  $\delta^{238}\text{U}$  values than coeval seawater (Chen et al., 2021;  
263 Clarkson et al., 2021). In contrast, carbonate sediments deposited under oxic bottom waters  
264 resulted in little to large increases in U content and  $\delta^{238}\text{U}$ , dominantly depending on the amount of  
265 pore water U(VI) reduction (Romaniello et al., 2013; Chen et al., 2018; Tissot et al., 2018;  
266 Clarkson et al., 2021). Thus, we first investigate the redox state of local depositional environments  
267 of ODP Hole 871C prior to discussion of the carbonate  $\delta^{238}\text{U}$  data.

268 Our Ce anomaly and RSE data suggest that carbonates from Hole 871C were deposited  
269 under oxic bottom waters with anoxic (but generally non-euxinic) pore waters below the sediment-  
270 water interface. The Ce/Ce\* was consistently lower than 0.5 throughout the whole carbonate  
271 section, indicating that these carbonates were deposited under oxic bottom waters and pore waters

272 (Haley et al., 2004). In contrast, the concentrations of V and Re in Hole 871C were moderately  
273 higher than in primary biogenic calcium carbonates (1 – 70 ppm vs. 0.01 – 0.5 ppm for V and 1 –  
274 7 ppb vs. <1 ppb for Re; Chen et al., 2018a; Romaniello et al., 2013), implying at least reducing  
275 pore waters below the sediment-water interface. Like V and Re, Hole 871C also documented  
276 significant enrichments of U, particularly over the PETM interval (~320 – 327 mbsf). The very  
277 low Mo concentrations in carbonates from Hole 871C (compared to primary biogenic carbonates  
278 0.01 – 0.1 ppm; Romaniello et al., 2016), on the other hand, suggest that the pore waters were non-  
279 euxinic. It should be noted that V, Mo, and U concentrations were the highest (67 ppm, 1.8 ppm,  
280 and 18.3 ppm) at 326.37 mbsf, suggesting likely euxinic pore waters.

281

## 282 **5.3 Alteration of $\delta^{238}\text{U}$ during carbonate diagenesis**

### 283 *5.3.1 Negative $\Delta^{238}\text{U}$ associated with a Mn oxide shuttle*

284 The lighter carbonate  $\delta^{238}\text{U}$  values between  $-0.47\text{‰}$  and  $-0.69\text{‰}$  over the PETM  
285 boundary (Fig. 4) are most likely associated with organic matter and manganese (Mn) oxides,  
286 rather than the expansion of global oceanic anoxia. Although multiple geochemical proxies ( $\delta^{34}\text{S}$   
287 in barite, I/Ca and  $\delta^{53}\text{Cr}$  in foraminifera, and abundances of Mn and U in carbonates) indicated  
288 heterogeneous oceanic deoxygenation over the PETM (Yao et al., 2018; Zhou et al., 2014, 2016;  
289 Chun et al., 2010; Rimmelzwaal et al., 2019), the extent of global oceanic anoxia cannot cause the  
290 extremely light carbonate  $\delta^{238}\text{U}$  values ( $-0.63\text{‰}$  and  $-0.69\text{‰}$ ) observed in ODP Hole 871C. These  
291 light U isotopic compositions are similar to  $\delta^{238}\text{U}$  values ( $\sim -0.7\text{‰}$ ) in carbonates of the end-  
292 Permian mass extinction interval (Brennecka et al., 2011; Lau et al., 2016; Zhang et al., 2018). The  
293 light end-Permian carbonate  $\delta^{238}\text{U}$  values were interpreted to result from an expansion of the  
294 anoxic seafloor to 20%. If our light carbonate  $\delta^{238}\text{U}$  values over PETM interval in ODP Hole 871C

295 were also caused by an expansion of oceanic anoxia, the predicted anoxic seafloor area would be  
296 ~ 20%. This prediction is inconsistent with Paleocene-Eocene pelagic carbonate  $\delta^{238}\text{U}$  values that  
297 suggested a maximum expansion of anoxic seafloor area to ~ 2% (Clarkson et al., 2021) as well  
298 as cGENIE model results which inferred that only 4% of the global ocean volume was anoxic over  
299 the PETM (Rommelzwaal et al., 2019). Furthermore, the high-resolution profiles of  $\delta^{238}\text{U}$  over the  
300 PETM interval (317 – 326 mbsf, Fig. 3E) revealed significant and abrupt fluctuations of carbonate  
301  $\delta^{238}\text{U}$  between  $-0.69\text{‰}$  and  $+0.71\text{‰}$  within a short time period of less than 200 kyr, conflicting  
302 with the lack of resolvable perturbation to the U cycle over this short time period (Clarkson et al.,  
303 2021).

304 Alternatively, our lighter carbonate  $\delta^{238}\text{U}$  values could be the consequence of an  
305 association with organic matter or Mn oxides. Organic matter preferentially uptakes  $^{235}\text{U}$  with an  
306 isotope fractionation of  $\sim 0.2\text{‰}$ , and uptake by organic matter has been proposed to explain the  
307 shift of  $\delta^{238}\text{U}$  in Paleocene-Eocene pelagic carbonates and modern organic-rich marine sediments  
308 to values lighter than coeval seawater (Chen et al., 2020; Clarkson et al., 2021; Abshire et al.,  
309 2019). Among all published U isotope data, only two modern organic-rich sediment samples (total  
310 organic carbon (TOC) = 8 and 9 wt%) from the anoxic shelf of Namibia had lighter  $\delta^{238}\text{U}$  values  
311 ( $-0.59$  and  $-0.62\text{‰}$ ) with high authigenic U concentrations of 5 and 10 ppm. However, the  
312 extremely low TOC content (less than 0.3 wt%; Premoli Silva et al., 1993) in our samples from  
313 Hole 871C cannot result in the accumulation of the high U concentrations of  $\sim 4 - 6$  ppm, ruling  
314 out the effects of organic matter on our  $\delta^{238}\text{U}$  data.

315 Experimental studies also demonstrated that Mn oxides preferentially adsorb  $^{235}\text{U}$ , with an  
316 isotope fractionation of  $\sim 0.2\text{‰}$  (Brennecka et al., 2011b; Dang et al., 2016; Jemison et al., 2016).  
317 The  $\sim 0.24\text{‰}$  isotopic offset between carbonate  $\delta^{238}\text{U}$  and coeval seawater at this depth is

318 consistent with that observed during U(VI) adsorption to Mn-oxides (Brennecka et al., 2011b;  
319 Dang et al., 2016; Jemison et al., 2016). A minor amount of pore-lining Mn oxide observed at a  
320 depth of ~317 mbsf of ODP Hole 871C (Wyatt et al., 1995) supports the argument that Mn oxides  
321 most likely lead to lighter carbonate  $\delta^{238}\text{U}$  than coeval seawater. It should be noted that these  
322 carbonate sediments have relatively high U concentrations, ~ 7 to 10 ppm. Manganese oxides  
323 affect carbonate  $\delta^{238}\text{U}$ , likely via a particulate Mn-shuttle proposed by Herrmann et al. (2018). The  
324 operation of a particulate Mn-shuttle can significantly increase U concentration but decrease  $\delta^{238}\text{U}$   
325 in carbonate sediments. Our redox-sensitive element concentrations and Ce/Ce\* data suggest a  
326 redoxcline below the sediment-water interface, favoring the active operation of a particulate Mn-  
327 shuttle (Algeo and Tribovillard, 2009). The reducing but non-sulfidic pore waters below the  
328 sediment-water interface (see Section 5.2) would dissolve Mn oxides, releasing soluble Mn back  
329 to bottom waters but scavenging the U sorbed to Mn oxides via reduction of U(VI) to insoluble  
330 U(IV).

331

### 332 *5.3.2 Positive $\Delta^{238}\text{U}$ induced by authigenic reduction of U(IV) in pore waters*

333 Diagenetic alteration of carbonate sediments at ODP Hole 871C leads to higher carbonate  
334  $\delta^{238}\text{U}$  values in bulk carbonate sediment relative to values expected for primary biogenic calcite  
335 grains (i.e., benthic foraminifera, echinoderms, and calcareous red algae) and in comparison to  
336 modern seawater (Fig. 5a). The isotopic offset between carbonate sediments and Paleogene  
337 seawater ( $\Delta^{238}\text{U}$ ) is  $0.59 \pm 0.24\%$  (N = 24,  $1\sigma$ ). The magnitude of this offset is significantly larger  
338 than the offset observed between Bahamian carbonate sediments that have a predominantly  
339 primary aragonitic mineralogy and modern seawater (Fig. 5b;  $\Delta^{238}\text{U} = 0.25 \pm 0.15\%$ , N = 162,  
340  $1\sigma$ ; Romaniello et al., 2013; Chen et al., 2018b; Tissot et al., 2018; Chen et al., 2018a; Livermore



341 et al., 2020). Furthermore, it is also observed that carbonate sediments from Hole 871C with  
342 positive  $\Delta^{238}\text{U}$  values show a positive correlation between increased  $\delta^{238}\text{U}$  values and U/Ca  
343 (Spearman's correlation coefficient:  $\rho = 0.47$ ,  $p$ -value = 0.02, Fig. 4).

344         Since carbonate sediments from Hole 871C were deposited under oxic bottom waters, the  
345 existence of carbonate  $\delta^{238}\text{U}$  values higher than modern seawater (Fig. 4) likely results from  
346 authigenic reductive accumulation of U(IV) in pore waters below the sediment-water interface  
347 during early diagenesis. Consistent with previous work on shallow-water platform carbonate  
348 sediments from the Bahamas (Chen et al., 2018b; Tissot et al., 2018), the significantly higher U  
349 concentrations in carbonate sediments in ODP Hole 871C compared to primary biogenic calcite  
350 precipitates (0.1 – 18 ppm vs. 0.01 – 0.11 ppm) likely results from dramatic authigenic enrichments  
351 of U(IV) during carbonate diagenesis. These authigenic phases containing U(IV), which  
352 preferentially accumulates  $^{238}\text{U}$  during U(VI) reduction, could lead to higher bulk carbonate  $\delta^{238}\text{U}$   
353 values compared to primary calcite grains. The 10- to 100-fold enrichments of authigenic U(IV)  
354 and significantly larger U isotope fractionation during U(VI) reduction to U(IV) than calcite  
355 coprecipitation with U(VI) (0.4 – 1.2‰ vs. 0 – 0.1‰; Basu et al., 2014; Stirling et al., 2015; Sytlo  
356 et al., 2015; Brown et al., 2018; Andersen et al., 2017; Chen et al., 2016, 2017, 2018a) can easily  
357 overprint the coeval seawater  $\delta^{238}\text{U}$  signals in biogenic calcites through the addition of cements  
358 during early diagenesis. Hence, we suggest that bulk carbonate  $\delta^{238}\text{U}$  values from Hole 871C  
359 (excluding samples with lighter  $\delta^{238}\text{U}$  values than coeval seawater) are predominantly controlled  
360 by the amount of authigenic U(IV), and so follow a general increasing trend with U/Ca.

361

362 *5.3.3 An authigenic U accumulation model for positive  $\Delta^{238}\text{U}$  in ODP Hole 871C*

363 To explore the effects of authigenic reduction of U(VI) in pore water below the sediment-  
 364 water interface on carbonate  $\delta^{238}\text{U}$  during diagenesis, we establish a simple geochemical model to  
 365 interpret the covariation of carbonate  $\delta^{238}\text{U}$  with U/Ca. This model assumes: (1) little or negligible  
 366 calcite dissolution and recrystallization occurred, due to the stability of primary calcite grains in  
 367 seawater; (2) reductive accumulation of U(IV) in pore waters below the sediment-water interface  
 368 during early diagenetic precipitation of calcite cements predominantly causes U isotope  
 369 fractionation during diagenesis; (3) U(VI) is incorporated into primary biogenic calcite with little  
 370 isotope fractionation (Fig. 6A; Chen et al., 2016, 2017, 2018a; Livermore et al., 2020). Under these  
 371 assumptions, carbonate  $\delta^{238}\text{U}$  in bulk carbonate sediments ( $\delta^{238}\text{U}_{\text{carb}}$ ) is, thus, determined by the  
 372 relative fractions of primary carbonate U ( $f_{\text{primary}}$ ) and authigenic U(IV) ( $f_{\text{auth}}$ ) added during  
 373 diagenesis. The  $\delta^{238}\text{U}$  value in the bulk carbonate sediments can be estimated by:

$$\delta^{238}\text{U}_{\text{carb}} = f_{\text{auth}} \times \delta^{238}\text{U}_{\text{auth}} + (1 - f_{\text{primary}}) \times \delta^{238}\text{U}_{\text{primary}} \quad (3)$$

374 where  $\delta^{238}\text{U}_{\text{primary}}$  and  $\delta^{238}\text{U}_{\text{auth}}$  are isotopic compositions of U in primary calcium carbonate  
 375 precipitates and authigenic U(IV) in carbonate sediments, respectively. Since U isotope  
 376 fractionation during primary calcium carbonate precipitation is little or negligible ( $< 0.1\%$ ; Chen  
 377 et al., 2018a; Livermore et al., 2020),  $\delta^{238}\text{U}_{\text{primary}}$  ( $= -0.39\%$ ) equals that of coeval seawater  
 378 ( $\delta^{238}\text{U}_{\text{sw}}$ ). Also, the isotopic composition of authigenic U(IV) can be described by:

$$\delta^{238}\text{U}_{\text{auth}} = \delta^{238}\text{U}_{\text{sw}} + \Delta^{238}\text{U}_{\text{auth-sw}} \quad (4)$$

379 where  $\Delta^{238}\text{U}_{\text{auth-sw}}$  is the isotope fractionation during U(VI) reduction to U(IV). Substituting Eq. 4  
 380 into Eq. 3, we can obtain

$$\delta^{238}\text{U}_{\text{carb}} = (1 - f_{\text{primary}}) \times \Delta^{238}\text{U}_{\text{auth-sw}} + \delta^{238}\text{U}_{\text{primary}} \quad (5)$$

381 The fraction of primary carbonate U in bulk carbonate sediments can be estimated as:

$$f_{\text{primary}} = \frac{\left(\text{U/Ca}\right)_{\text{primary}}}{\left(\text{U/Ca}\right)_{\text{carb}}} \quad (6)$$

382 Substituting Eq. 6 into Eq. 5, we can obtain

$$\delta^{238}\text{U}_{\text{carb}} = \left[ 1 - \frac{\left(\text{U/Ca}\right)_{\text{primary}}}{\left(\text{U/Ca}\right)_{\text{bulk}}} \right] \times \Delta^{238}\text{U}_{\text{auth-sw}} + \delta^{238}\text{U}_{\text{primary}} \quad (9)$$

383 Equation 9 reveals that carbonate  $\delta^{238}\text{U}$  in bulk carbonate sediments depends on the relative  
 384 fraction of authigenic U(IV) ( $f_{\text{IV}}$  defined in Eq. 8) and the magnitude of isotope fractionation  
 385 ( $\Delta^{238}\text{U}_{\text{auth-sw}}$ ) during authigenic reduction of U(VI) to U(IV). Since ODP Hole 871C (this study)  
 386 and coeval pelagic carbonates (ODP sites 690, 401, and 865 from Clarkson et al. (2021)) have a  
 387 predominantly primary calcitic mineralogy, we assume carbonates with  $\delta^{238}\text{U}$  close to  
 388 contemporaneous seawater preserve the Paleocene-Eocene primary calcite U/Ca, ranging from ~  
 389 0.02 to 0.10  $\mu\text{mol/mol}$  (Fig. 6A), which is higher than U/Ca in foraminiferal calcite in modern  
 390 oceans (e.g., 0.01 – 0.02  $\mu\text{mol/mol}$ ; Keul et al., 2013). The higher U/Ca in these Paleocene-Eocene  
 391 foraminiferal calcite likely results from the significantly lower seawater  $[\text{CO}_3^{2-}]$  in Paleocene-  
 392 Eocene seawater relative to modern oceans (~100  $\mu\text{mol/mol}$  vs. ~200  $\mu\text{mol/mol}$ ; Zeebe and Tyrrell,  
 393 2019). The U/Ca in foraminiferal calcite is predominantly controlled by seawater chemistry and  
 394 increases significantly with seawater  $[\text{CO}_3^{2-}]$  (Russell et al., 2004; Allen et al., 2016; Keul et al.,  
 395 2013; Chen, 2020). The  $\Delta^{238}\text{U}_{\text{auth-sw}}$  during abiotic and biotic U(VI) reduction varied between 0.4  
 396 to 1.2‰, depending on the U reduction kinetics and aqueous U speciation (Basu et al., 2014, 2020;  
 397 Brown et al., 2018; Wang et al., 2015; Stylo et al., 2015; Stirling et al., 2015).

398 According to our model, the predicted range of carbonate  $\delta^{238}\text{U}$  (gray area in Fig. 6A)  
 399 during diagenesis can cover nearly all the  $\delta^{238}\text{U}$  values ( $> -0.39\text{‰}$ ) in Paleocene-Eocene

400 carbonates (this study and Clarkson et al. (2021), Fig. 6A) when  $\Delta^{238}\text{U}_{\text{auth-sw}}$  varies between +0.4  
401 to +0.8‰. The two data points with extremely high  $\delta^{238}\text{U}$  values (+0.71 and +0.73‰) likely result  
402 from a larger  $\Delta^{238}\text{U}_{\text{auth-sw}}$  of  $\sim +1.2\text{‰}$ . Our model suggests that authigenic accumulation of U(IV)  
403 is the predominant factor controlling carbonate  $\delta^{238}\text{U}$  with positive isotopic offsets (relative to  
404 coeval seawater) during diagenesis, accounting for the general increasing trend of carbonate  $\delta^{238}\text{U}$   
405 with U/Ca.

406

#### 407 **5.4 $\delta^{238}\text{U}$ in calcite is more sensitive to diagenesis than aragonite**

408 Our work and previous studies reveal that  $\delta^{238}\text{U}$  and U/Ca in primary calcite is more  
409 susceptible to diagenetic alterations as compared to primary aragonite. Specifically, foraminiferal  
410 calcite admixed with Mn oxides or organic matter led to a negative shift of  $\sim -0.2\text{‰}$  in carbonate  
411  $\delta^{238}\text{U}$  from coeval Paleocene-Eocene seawater (Clarkson et al., 2021; Fig. 4 *this study*). Modern  
412 microbial calcite deposited under sulfidic bottom waters of the redox-stratified Fayetteville Green  
413 Lake (New York, USA) also caused a U isotope fractionation of  $\sim +0.6\text{‰}$  relative to the bottom  
414 water of this lake (Chen et al., 2021). The Paleocene-Eocene foraminiferal calcite deposited under  
415 suboxic to anoxic bottom waters resulted in a U isotopic offset of +0.4 to +0.6‰ relative to  
416 contemporaneous seawater (Clarkson et al., 2021). Our data further demonstrates that primary  
417 calcite deposited under oxic bottom waters and alongside reducing but non-sulfidic pore water can  
418 also lead to positive U isotopic offsets of  $0.59 \pm 0.24\text{‰}$  (N = 24, 1 $\sigma$ ) due to authigenic reductive  
419 accumulation of U(IV) in pore water below the sediment-water interface. The average U/Ca in  
420 carbonate sediments with  $\delta^{238}\text{U}$  values higher than in modern seawater was  $1.03 \pm 1.60 \mu\text{mol/mol}$   
421 (N = 46, 1 $\sigma$ ), which was generally one order of magnitude higher than in primary calcite  
422 (predominantly foraminifera with an average value of  $0.06 \pm 0.04 \mu\text{mol/mol}$ , N = 48, 1 $\sigma$ ; Clarkson

423 et al., 2021; Chen, 2020). Briefly, diagenesis of primary calcite precipitates can result in negative  
424 U isotopic offsets ( $-0.18 \pm 0.09\%$ ,  $N = 13$ ,  $1\sigma$ ) due to Mn oxides and positive offsets ( $+0.50 \pm$   
425  $0.22\%$ ,  $N = 46$ ,  $1\sigma$ ) because of authigenic reductive accumulation of U(IV) in sulfidic water  
426 columns and below the sediment-water interface. Additionally, these positive offsets generally  
427 increased with U/Ca (Fig. 6A), which can be described by the authigenic reductive accumulation  
428 model (see Section 5.3.3).

429 In contrast, modern Bahamian shallow-water platform carbonate sediments that have a  
430 predominantly primary aragonitic mineralogy tend to have a tighter range in  $\delta^{238}\text{U}$  with a much  
431 smaller U isotopic offset of  $+0.25 \pm 0.15\%$  ( $N = 162$ ,  $1\sigma$ ; Fig. 4 B and Fig. 6B) relative to modern  
432 seawater (Romaniello et al., 2013; Chen et al., 2018b; Tissot et al., 2018). The mean value of U/Ca  
433 in these carbonate sediments was  $2.20 \pm 0.95 \mu\text{mol/mol}$  ( $N = 162$ ,  $1\sigma$ ), which was about 3-fold  
434 higher than that in primary aragonite (corals and calcareous green algae with an average value of  
435  $0.79 \pm 0.46 \mu\text{mol/mol}$ ,  $N = 39$ ,  $1\sigma$ ) in modern oceans (Romaniello et al., 2013; Chen et al., 2018a,  
436 b; Tissot et al., 2018; Livermore et al., 2020). The variation of  $\delta^{238}\text{U}$  with U/Ca in these carbonate  
437 sediments did not follow the increasing trend (Fig. 6B;  $\rho = 0.04$ ,  $p\text{-value} = 0.61$  for spearman  
438 correlation) as observed in carbonate sediments that have a primary calcitic mineralogy (Fig. 6A;  
439  $\rho = 0.66$ ,  $p\text{-value} < 0.01$ ).

440 The more sensitive response of  $\delta^{238}\text{U}$  and U/Ca in primary calcite to the influence of  
441 diagenesis relative to primary aragonite most likely results from the significantly lower U/Ca in  
442 calcite. If we assume that pore water U(VI) reduction below the sediment-water interface can  
443 produce  $\sim 1.6$  ppm U(IV) during diagenesis, the quantity of U(IV) is about 1 – 2 orders of  
444 magnitude greater than that in primary calcite (0.2 – 30 ppb; e.g., Allen et al., 2016), and  
445 approximately 0.7 – 4 times of that in primary aragonite (0.4 – 2.4 ppm; e.g., Romaniello et al.,

446 2013; Livermore et al., 2020). As a result, the original U in primary calcite would account for ~  
447 2% of the total U in carbonate sediments after cementation, whereas U in primary aragonite would  
448 be ~ 20 – 40% of the total U in bulk carbonate sediments. Obviously, authigenic reductive  
449 accumulation of U(IV) could more easily overprint the original U isotope signature in primary  
450 calcite as compared to primary aragonite, producing a general increasing trend of  $\delta^{238}\text{U}$  with U/Ca  
451 (Fig. 6A) in carbonate sediments that started with a primary calcitic mineralogy.

452 Similarly, the lower U concentration in primary calcite makes carbonate  $\delta^{238}\text{U}$  more  
453 susceptible to the effect of Mn oxides than primary aragonite. Ferromanganese crust and nodules  
454 in modern oceans typically have U concentrations of ~ 10 ppm (Hein and Koschinsky, 2013),  
455 which is about three orders of magnitude larger than in the primary foraminiferal calcite (~ 27 ±  
456 23 ppb; Russell et al., 2004; Keul et al., 2013; Allen et al., 2016; Chen, 2020). As a result, the  
457 admixture of Mn oxides with primary calcite (Clarkson et al., 2021; Herrmann et al., 2018) can  
458 easily cause negative shifts in carbonate  $\delta^{238}\text{U}$  during carbonate diagenesis. In contrast, primary  
459 aragonite and Mn oxides in modern oceans have the same order of magnitude in U concentration,  
460 making  $\delta^{238}\text{U}$  in carbonate sediments that have a primary aragonitic mineralogy more resistant to  
461 diagenetic alterations due to Mn oxides.

462 In summary,  $\delta^{238}\text{U}$  of bulk carbonate sediments dominated by primary calcite grains are  
463 more sensitive to diagenesis compared to aragonite-bearing equivalents because calcite typically  
464 has significantly lower U concentrations than aragonite. Variations of  $\delta^{238}\text{U}$  in bulk carbonate  
465 sediments that have a primary calcitic mineralogy more likely reflect the redox state of local early  
466 diagenetic environments, to first order, and require careful screening in order to be used as  
467 indicators of global seawater U isotope signatures (see the discussion below). Carbonate sediments  
468 with low U/Ca that is closer to that of primary calcite are more likely to represent seawater  $\delta^{238}\text{U}$

469 (Fig. 6 A), although carbonate  $\delta^{238}\text{U}$  is still likely to be affected by Mn oxides and organic matter  
470 that can result in limited negative offsets ( $< 0.2\text{‰}$ ) from coeval seawater.

471

## 472 **5.5 Cross-correlations of U/Ca, $\delta^{238}\text{U}$ , and traditional diagenetic indicators of carbonates**

473 Our results reveal a positive correlation ( $\rho = 0.47$ ,  $p$ -value = 0.02 for spearman correlation)  
474 between  $\delta^{238}\text{U}$  and U/Ca in carbonate sediments from ODP Hole 871C, whereas these two  
475 geochemical signals show statistically insignificant correlations with traditional diagenetic  
476 indicators (e.g.,  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{18}\text{O}_{\text{carb}}$ , Sr/Ca, Mg/Ca, and Mn/Sr) and cerium anomaly (Ce/Ce\*) (Fig.  
477 7). Since calcite typically has low U concentration ( $< 100$  ppb), authigenic U(IV) during diagenesis  
478 dominates over U in primary calcite and leads to the positive correlation between U/Ca and  $\delta^{238}\text{U}$ .

479 Unlike carbonate sediments from ODP Hole 871C, the platform carbonate sediments from  
480 the Bahamas show statistically insignificant correlation between U/Ca and  $\delta^{238}\text{U}$  and have a  
481 predominantly primary aragonitic mineralogy (Chen et al., 2018a; Tissot et al., 2018). This  
482 insignificant correlation most likely results from the decoupling of U/Ca from  $\delta^{238}\text{U}$  during  
483 carbonate mineralogy transformations (*i.e.*, aragonite to calcite transition). Carbonate sediments  
484 from the Bahamas have undergone extensive aragonite-to-calcite transformation and significant  
485 authigenic enrichments of U(IV) (Chen et al., 2018a; Tissot et al., 2018; Romaniello et al., 2013).  
486 Aragonite-to-calcite transformation during meteoric diagenesis of a *Orbicella annularis* coral head  
487 from the Pleistocene Key Largo Limestone resulted in  $\sim 50\%$  decrease in U/Ca but no changes in  
488  $\delta^{238}\text{U}$  values (Chen et al., 2018a). Abiotic calcium carbonate coprecipitation experiments also  
489 demonstrated much lower U concentration in aragonite compared to calcite ( $\sim 2200$  ppm vs.  $\sim 350$   
490 ppm) but negligible difference in  $\delta^{238}\text{U}$  in these two carbonate minerals (Chen et al., 2016). As a  
491 result, the decoupling of U/Ca from  $\delta^{238}\text{U}$  during aragonite-to-calcite transformation breaks down

492 the positive correlation between U/Ca and  $\delta^{238}\text{U}$  due to authigenic accumulation of U(IV) in  
493 diagenetic alteration of pristine aragonite. In short, U/Ca is governed by both carbonate mineralogy  
494 and porewater U reduction during diagenesis of carbonate sediments from the Bahamas, whereas  
495  $\delta^{238}\text{U}$  in the same carbonates sediments is predominantly controlled by porewater U reduction.

496 Since  $\delta^{238}\text{U}$  in carbonate sediments predominantly depends on porewater U reduction,  
497 carbonate  $\delta^{238}\text{U}$  from the Bahamas (Chen et al., 2018a; Tissot et al., 2018) and ODP Hole 871C  
498 do not show significant correlations with traditional diagenetic indices for changes in carbonate  
499 morphology (e.g., recrystallization from aragonite to calcite (Sr/Ca), dolomitization (Mg/Ca)),  
500 meteoric diagenesis ( $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$ ), and the extent of diagenetic alterations of carbonates  
501 (Mn/Sr). These findings caution against using these traditional diagenetic indicators to argue for  
502 the well-preservation of  $\delta^{238}\text{U}$  values during carbonate diagenesis.

503

## 504 **5.6 Implications for carbonate $\delta^{238}\text{U}$ as a global paleoredox proxy**

505 The higher sensitivity of  $\delta^{238}\text{U}$  in primary calcite (relative to primary aragonite) during  
506 diagenesis suggests that caution should be exercised when interpreting carbonate  $\delta^{238}\text{U}$  data from  
507 carbonate sediments that have a primary calcitic mineralogy to reconstruct the past global redox  
508 conditions of oceans. It is essential to first identify the original carbonate mineralogy (aragonite or  
509 calcite) using geochemical indicators such as Sr/Ca. If the original mineralogy was calcite, it is  
510 then crucial to determine the redox state of the local depositional environments using  
511 biogeochemical proxies such as cerium anomalies, I/Ca, redox-sensitive elements (Mo, Re, and  
512 Mn), and benthic foraminiferal assemblages (e.g., Loubere, 1996; Tostevin et al., 2016; Lu et al.,  
513 2010). When primary calcite precipitates were deposited under anoxic bottom waters, the original  
514 carbonate  $\delta^{238}\text{U}$  would be completely overprinted in bulk sediments by the relatively high U-



515 bearing diagenetic phases and, consequently, altered to be heavier than coeval seawater thereby  
516 only reflecting the local redox conditions (Fig. 6A, Chen et al., 2021; Clarkson et al., 2021). Under  
517 oxic depositional conditions, carbonate sediments that have low U/Ca values close to those of  
518 primary calcite precipitates ( $< 0.10 \mu\text{mol/mol}$ , e.g., Russell et al., 2004) most likely capture global  
519 seawater  $\delta^{238}\text{U}$ , whereas carbonate sediments with high U/Ca ( $> 0.10 \mu\text{mol/mol}$ , *i.e.*, ODP Hole  
520 871C this study) tend to reflect the effects of local diagenetic alterations on  $\delta^{238}\text{U}$ .

521         If the original carbonate mineralogy was aragonite,  $\delta^{238}\text{U}$  in bulk carbonate sediments (e.g.,  
522 modern Bahamian shallow-water platform carbonate sediments) would record U isotopic  
523 compositions that are close or heavier than coeval seawater  $\delta^{238}\text{U}$  after diagenesis (Chen et al.,  
524 2018b; Tissot et al., 2018). Since U concentration in aragonite is significantly higher than calcite  
525 and comparable to the concentrations achieved through authigenic reductive accumulation of  
526 U(IV) during early diagenesis,  $\delta^{238}\text{U}$  in bulk carbonate sediments that were originally aragonite in  
527 composition are less sensitive to the degree of diagenetic alteration and more likely exhibit  
528 consistent positive isotopic offsets from coeval seawater (e.g.,  $\sim 0.25 \pm 0.15\%$  in Bahamian  
529 carbonate sediments). Thus, we argue that  $\delta^{238}\text{U}$  in bulk carbonate sediments that have a primary  
530 aragonitic mineralogy are more likely to record changes in coeval seawater  $\delta^{238}\text{U}$  and global  
531 oceanic redox conditions.

532

## 533 **6. Conclusions**

534         We observed larger positive and negative fluctuations of carbonate  $\delta^{238}\text{U}$  values (relative  
535 to modern seawater) in shallow-water Paleocene-Eocene carbonate sediments that have a primary  
536 calcitic mineralogy and deposited under oxic bottom waters, suggesting that  $\delta^{238}\text{U}$  in primary  
537 calcite is more susceptible to carbonate diagenesis compared to primary aragonite. Our work

538 implies that variations of  $\delta^{238}\text{U}$  in carbonate sediments that have a primary calcitic mineralogy  
539 more likely reflects the redox state of pore waters. These carbonate sediments that have U/Ca  
540 values close to primary calcite more likely record and preserve seawater  $\delta^{238}\text{U}$ . Thus, it is essential  
541 to identify the original carbonate mineralogy (aragonite or calcite) and constrain the local  
542 depositional conditions of carbonates when interpreting carbonate  $\delta^{238}\text{U}$  data and applying it to  
543 reconstruct the global redox conditions of oceans through time.

544

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549

#### 550 **Appendix A. Supplementary data**

551 Supplementary data to this article can be found online at ...

552

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750



751 **Figure Captions**

752

753 **Figure 1.** (A) Paleogeographic reconstruction of 56 Ma ([www.odsn.de](http://www.odsn.de)) with ODP site 871 marked  
754 (B) and contoured bathymetry of Limalok Guyot and ODP Site 871 (from Premoli Silva et al.,  
755 1993). The contour interval in panel B is 250 m.

756

757

758 **Figure 2.** Abundance of redox-sensitive elements V (A), Mo (B), Re (C) and U (D), and Ce  
759 anomaly (Ce/Ce\*, E) in shallow-water carbonates from Hole 871C. The stratigraphy is based on  
760 benthic forams (Premoli Silva et al., 1993). The dashed blue line represents Ce/Ce\* = 0.5. When  
761 Ce/Ce\* is below 0.5, it indicates bottom waters are oxic (Haley et al., 2004).

762

763

764 **Figure 3.**  $\delta^{13}\text{C}_{\text{carb}}$  (A),  $\delta^{18}\text{O}_{\text{carb}}$  (B), U concentration (C), and  $\delta^{238}\text{U}$  (D) in shallow-water carbonate  
765 sediments from ODP Hole 871C. High-resolution  $\delta^{238}\text{U}$  in carbonates over the PETM from ODP  
766 cores 144-871C-23R and -22R (E). The blue dashed line represents  $\delta^{238}\text{U}$  of modern seawater  
767 ( $-0.39\text{‰}$ ; Andersen et al., 2015; Tissot and Dauphas, 2015). ‘mbsf’ stands for meters below  
768 seafloor. The carbon and oxygen isotope data are from Robinson (2011). The error bars represent  
769 twice standard deviations of the sample or the long-term reproducibility of the reference standard  
770 CRM-145a, whichever is larger.

771

772

773 **Figure 4.** Cross plot of carbonate  $\delta^{238}\text{U}$  versus U/Ca in carbonate sediments (ODP Hole 871C)  
774 derived mainly from primary biogenic calcite. The horizontal gray band represent the seawater  
775  $\delta^{238}\text{U}$  value ( $-0.392 \pm 0.005\text{‰}$ ; Tissot et al., 2015). The error bars are the twice standard deviation  
776 of replicate measurements of each sample or the long-term reproducibility the reference standard  
777 CRM-145a, whichever is larger. The data for Spearman correlation only consider samples with  
778  $\delta^{238}\text{U}$  values higher than modern seawater.

779

780

781 **Figure 5.** Histograms of  $\delta^{238}\text{U}$  in primary biogenic calcite (yellow; brachiopods, red algae, and  
782 echinoderm) and aragonite (red; corals and green algae) and shallow-water carbonate sediments  
783 derived mainly from biogenic calcite (‘Calcite-origin’, grey; this study) and aragonite (‘Aragonite-  
784 origin’, blue) in modern oceans (Chen et al., 2018b, 2018b; Romaniello et al., 2013; Tissot et al.,  
785 2018; Livermore et al., 2020). The dashed pink lines represent seawater  $\delta^{238}\text{U}$ . The arrows stand  
786 for the magnitude of the isotopic offsets between carbonate sediments and modern seawater.

787

788 **Figure 6.** Cross plots of carbonate  $\delta^{238}\text{U}$  versus U/Ca in primary calcite (orange symbols;  
789 brachiopods, corals, red algae, echinoderm, and foraminifera) and aragonite (gray symbols; corals  
790 and calcareous green algae), and carbonate sediments that have a primary calcitic (‘Calcite-origin’,  
791 blue and pink symbols, A) and aragonitic (‘Aragonite-origin’, white symbols, B) mineralogy in  
792 modern oceans (Chen et al., (2018a, 2018b), Livermore et al., (2020); Romaniello et al., (2013);  
793 Clarkson et al., (2021); Tissot et al., (2018)). **The horizontal gray band represent the seawater  $\delta^{238}\text{U}$   
794 value ( $-0.392 \pm 0.005 \text{‰}$ ; Tissot et al., 2015). The error bars are 2 SD of samples.** The gray areas  
795 in panels A and B represent the range of carbonate  $\delta^{238}\text{U}$  based on the authigenic enrichment model

796 in Section 5.3.2 when the isotope fractionation during U reduction ranges between +0.4 and +0.8‰  
797 when the U/Ca ratios in primary calcite and aragonite vary between ~ 0.03 and 0.12 μmol/mol and  
798 between ~ 0.2 and 1.0 μmol/mol, respectively. The spearman correlation coefficient  $\rho$  and  $p$ -value  
799 are listed in panels A and B. Only carbonate samples that have  $\delta^{238}\text{U}$  values higher than modern  
800 seawater were used for spearman correlation analysis.

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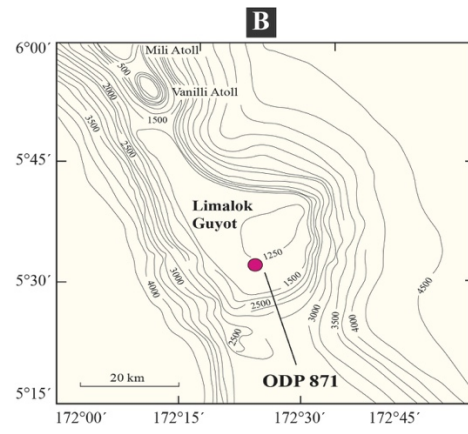
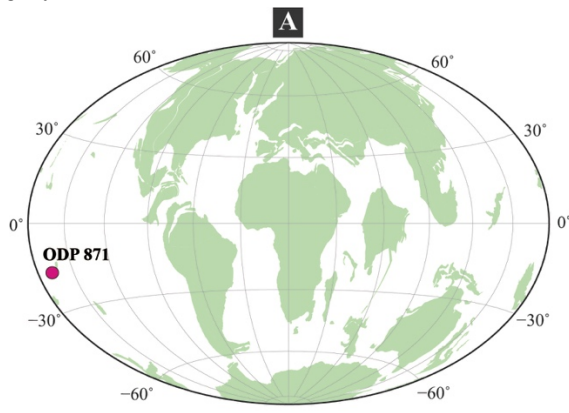
803 **Figure 7.** Cross plots of U/Ca,  $\delta^{238}\text{U}$ , Ce/Ce\*, and diagenetic parameters (Sr/Ca, Mg/Ca, Mn/Sr,  
804  $\delta^{13}\text{C}_{\text{carb}}$ , and  $\delta^{18}\text{O}_{\text{carb}}$ ) for ODP Hole 871C. Spearman's rank values ( $\rho$ ,  $p$ -value) are displayed in  
805 each panel. Panels with full colors indicates statistically significant correlations (*i.e.*,  $p$ -value <  
806 0.05); panels with transparent colors represent non-significant correlations. Blue and red symbols  
807 represent carbonate  $\delta^{238}\text{U}$  values higher and lower than modern seawater  $\delta^{238}\text{U}$  (-0.39‰; Tissot  
808 and Dauphas, 2015). Samples with  $\delta^{238}\text{U}$  values lower than modern seawater were not included  
809 in spearman correlation analysis. The  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  data were from Robinson (2011).  
810

811 Table 1. Summary of elemental ratios (Sr/Ca, Mg/Ca, U/Ca, and Mn/Sr), stable isotopic  
 812 compositions ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{238}\text{U}$ ), and cerium anomaly in ODP Hole 871C

Sample ID	Depth mbsf	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	$\delta^{238}\text{U}$ ‰	2 SD ‰	Sr/Ca mmol/mol	Mg/Ca mmol/mol	Mn/Sr mol/mol	U/Ca mmol/mol	Ce/Ce*
LIM 90	153.00	1.7	-1.6	0.47	0.10	0.37	24.26	0.18	2.18	0.34
LIM 103	172.60	0.8	-2.1	-0.19	0.13	0.34	24.30	0.07	0.09	0.28
LIM 110	191.55	0.7	-2.2	0.13	0.10	0.22	22.34	0.04	0.39	0.35
LIM 115	201.35	-0.8	-3.8	0.22	0.10	0.28	26.78	0.08	1.01	0.36
LIM 123	211.00	0.6	-4.2	0.26	0.10	0.22	26.05	0.04	0.72	0.40
LIM 132	249.70	1.0	-1.6	0.35	0.13	0.27	18.22	0.01	0.27	0.29
LIM 2	268.85	-0.2	-3.8	0.07	0.10	0.21	16.20	0.02	0.31	0.27
LIM 5	278.11	-0.1	-3.6	-0.10	0.10	0.22	20.05	0.02	0.28	0.30
LIM 9	297.25	-0.2	-3.8	0.26	0.10	0.31	24.36	0.01	0.60	0.26
LIM 28	317.25	1.5	-0.9	-0.59	0.11	0.27	22.83	0.02	5.63	0.19
LIM 47	326.21	1.0	-0.8	0.47	0.11	0.28	22.24	0.01	3.37	0.21
LIM 48	326.26	1.4	0.4	-0.47	0.10	0.28	23.10	0.02	5.88	0.19
LIM 49	326.32	1.0	-1.3	-0.47	0.11	0.29	24.01	0.03	4.03	0.20
LIM 50	326.37	1.3	-1.1	0.64	0.10	0.29	20.14	0.02	9.92	0.19
LIM 51	326.42	0.7	-1.2	-0.69	0.10	0.20	21.91	0.03	4.55	0.23
LIM 53	335.80	1.5	-1.7	-0.49	0.10	0.26	22.89	0.03	4.88	0.23
LIM 54	335.85	-1.3	-3.8	-0.02	0.10	0.35	22.42	0.01	0.81	0.19
LIM 56	335.95	-0.5	-2.6	-0.01	0.11	0.21	23.32	0.01	0.38	0.23
LIM 60	336.15	0.9	0.8	0.38	0.11	0.22	21.20	0.01	0.18	0.25
LIM 63	336.30	1.6	-1.2	0.71	0.10	0.27	24.65	0.01	4.09	0.19
LIM 66	345.40	0.8	-2.3	-0.09	0.10	0.21	18.90	0.01	0.96	0.19
LIM 67	355.10	1.8	-0.4	0.33	0.12	0.17	18.70	0.04	0.35	0.22
LIM 70	355.25	1.6	-1.2	0.03	0.11	0.20	20.02	0.03	0.20	0.24
LIM 73	364.75	1.8	-1.1	0.03	0.10	0.25	21.19	0.04	0.39	0.23
LIM 75	374.35	1.8	-1.2	0.39	0.10	0.23	18.53	0.03	2.51	0.17
LIM 155	384.70	1.8	-0.7	0.17	0.11	0.25	19.32	0.06	1.27	0.23
LIM 163	393.50	1.4	-1.1	0.25	0.11	0.26	21.64	0.14	0.23	0.30
LIM 179	404.00	1.9	-0.9	0.03	0.11	0.25	19.93	0.06	2.17	0.28
LIM 185	412.90	1.2	-1.1	0.39	0.10	0.29	21.33	0.01	0.32	0.23

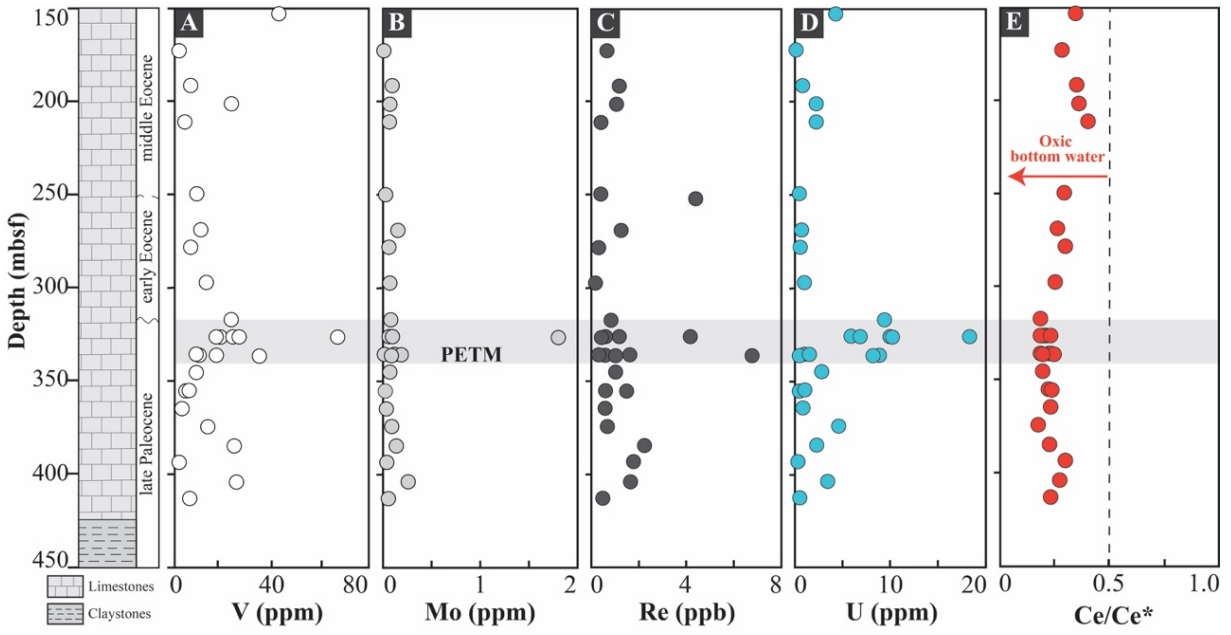
813 Note:  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  were from Robinson (2011).

815 **Figure 1.**



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817 **Figure 2.**



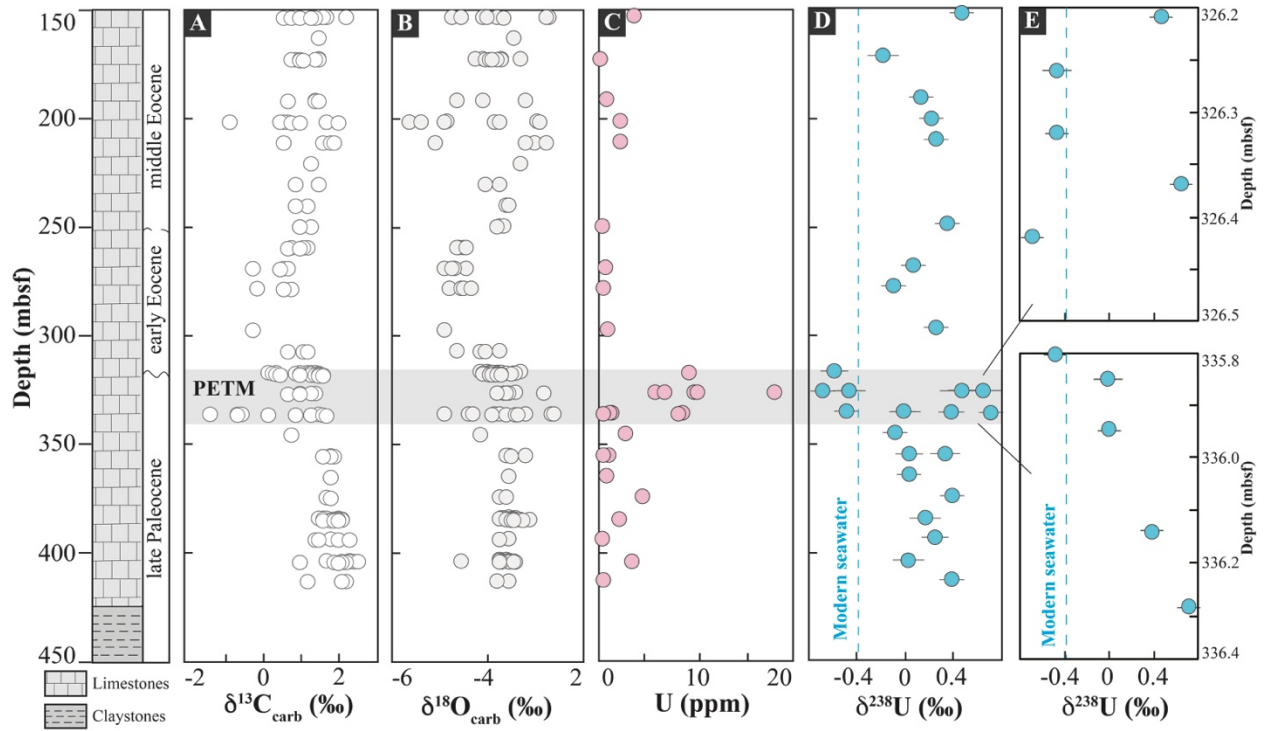
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822 **Figure 3.**

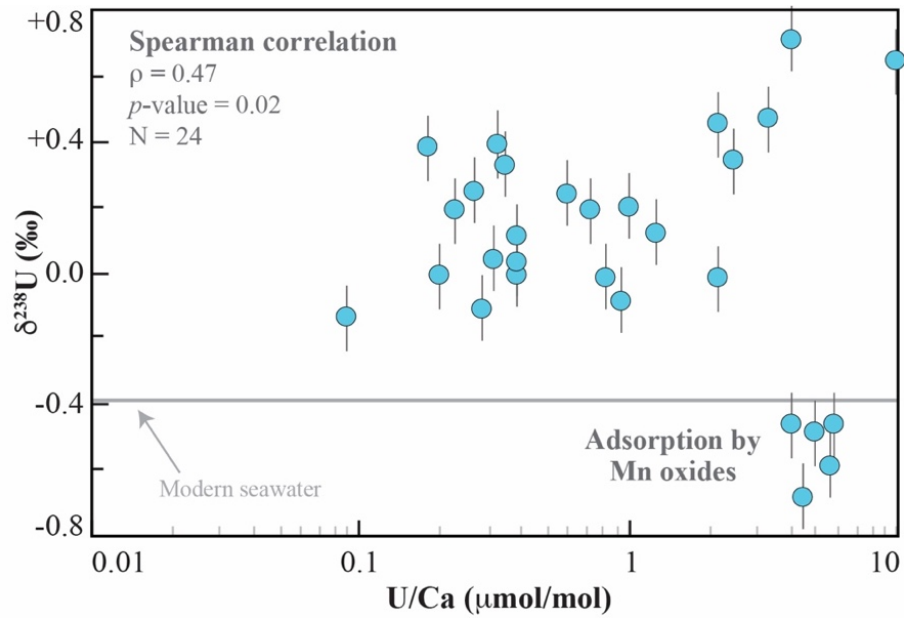


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826 **Figure 4.**

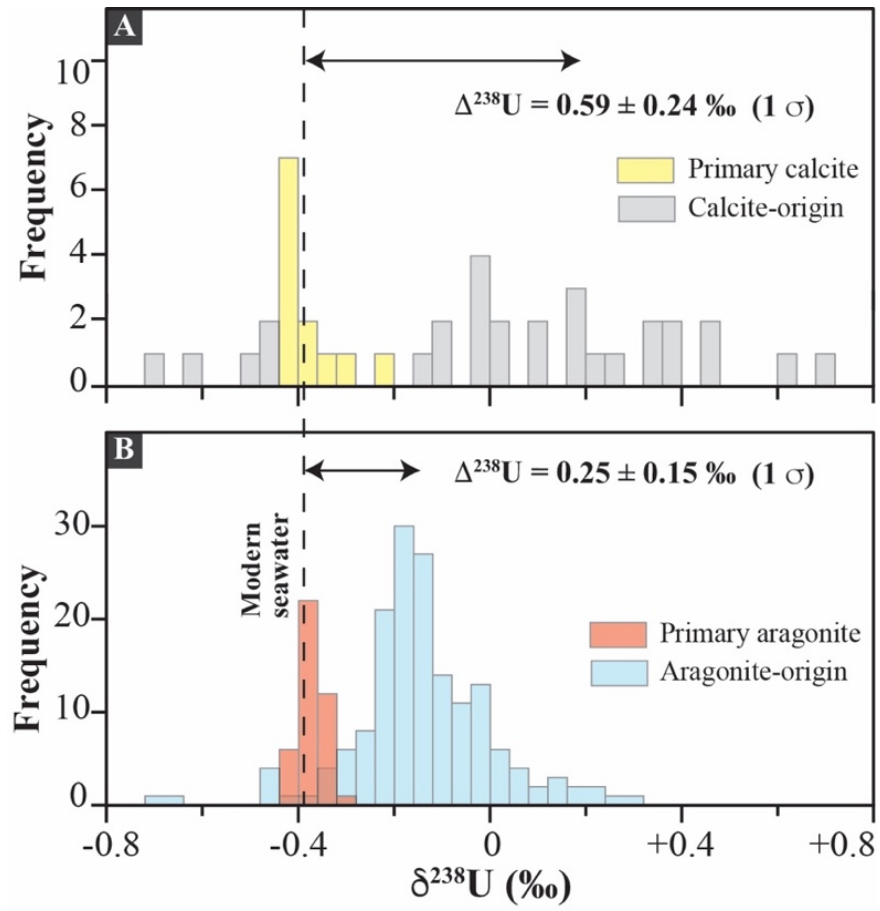


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830 **Figure 5.**



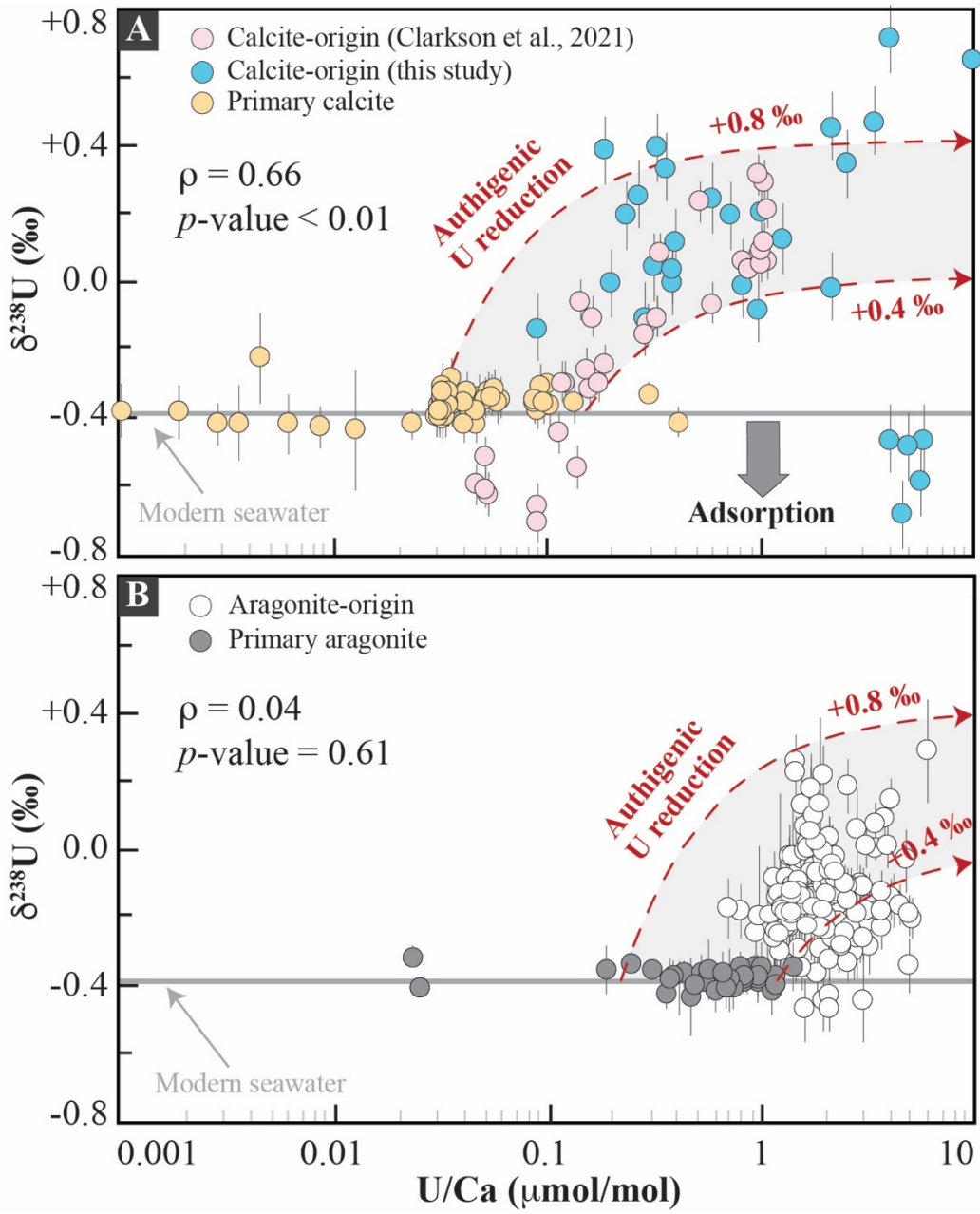
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834 **Figure 6.**



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837 **Figure 7**

