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Highly dynamic marine redox states through the Cambrian explosion

highlighted by authigenic $\delta^{238}\text{U}$ records

Guang-Yi Wei^{1,2*}, Noah J. Planavsky², Lidya G. Tarhan², Tianchen He³, Dan Wang⁴,

Graham A. Shields⁵, Wei Wei⁶, Hong-Fei Ling^{1*}

¹*State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, China*

²*Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA*

³*School of Earth and Environment, University of Leeds, Leeds, U.K.*

⁴*School of Geographic Science, Nantong University, Nantong 226019, China*

⁵*Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, U.K.*

⁶*CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Anhui 230026, China*

*Guang-Yi Wei (guangyiwei@nju.edu.cn); Hong-Fei Ling (hfling@nju.edu.cn)

Abstract

The history of oceanic oxygenation from the late Neoproterozoic to the early Cambrian is currently debated, making it difficult to gauge whether, and to what extent environmental triggers played a role shaping the trajectory of metazoan diversification. Uranium isotope ($\delta^{238}\text{U}$) records from carbonates have recently been used to argue for significant swings in the global marine redox states from the late Neoproterozoic to the early Cambrian. However, geochemical signatures in carbonates—the U isotope archive most commonly employed to argue for redox shifts—are susceptible to diagenetic alteration and have variable offsets from seawater values. Therefore, there is an impetus to reconstruct seawater U isotopic evolution using another sedimentary archive, in order to crosscheck that these excursions can indeed be linked to global shifts in marine redox landscape. Here we

29 report new U isotope data from two fine-grained siliciclastic upper Ediacaran to lower
30 Cambrian (ca. 551 Ma–515 Ma) successions in South China. We find large $\delta^{238}\text{U}$
31 swings between -0.63‰ and +0.39‰ for calculated values of authigenic U in the
32 siliciclastic rocks, consistent with correlative records from the carbonates. The
33 replication of these patterns in both carbonate and siliciclastic units provides
34 confirmatory~~compelling~~ evidence that the early Cambrian seawater was characterized
35 by ~~did indeed experiences~~ highly ~~variable~~ variable U isotope compositions ~~marine~~
36 ~~redox conditions~~. These new $\delta^{238}\text{U}$ data also provide higher-resolution records of
37 global oceanic redox during ~~the~~ Cambrian Age 3, coeval with a critical interval of the
38 Cambrian explosion. These $\delta^{238}\text{U}$ data bolster the case that the Ediacaran-Cambrian
39 transition ~~did indeed~~ experienced massive swings in marine redox state, providing a
40 dynamic environmental backdrop for and potentially even a key driver of the
41 emergence and radiation of metazoans.

42 **Keywords**

43 uranium isotopes; siliciclastic strata; early Cambrian; marine redox dynamics; animal
44 innovations

45 **1. Introduction**

46 There has been longstanding debate over~~regarding~~—_ whether the
47 Ediacaran–Cambrian emergence and diversification of metazoans coincided with
48 progressive oxidation of the ocean-atmosphere system and, if so, to what extent this
49 environmental transition may have directly influenced the trajectory or pace of

50 metazoan evolution (Och and Shields-Zhou, 2012; Lyons et al., 2014; Sperling et al.,
51 2013, 2015). In contrast to the standard view of a largely unidirectional redox
52 transition, several recent studies have suggested that, during the interval spanning the
53 | Ediacaran to the early Cambrian, pulses~~ed episodes~~ of widespread marine anoxia were
54 common and recurrent (Wei et al., 2018; Wood et al., 2018; Zhang et al., 2018, 2019;
55 | Tostevin et al., 2019; Dahl et al., 2019). Building upon~~from~~ this emerging record of
56 environmental variability, it has been suggested that temporally and spatially dynamic
57 environmental conditions, rather than stymying the emergence of complex life,
58 actually spurred the development and dissemination of biotic novelties, and thus the
59 | rapid diversification, and~~and~~ turnover and ecosystem restructuring characteristic of this
60 interval (Wei et al., 2018; Wood and Erwin, 2018; Wood et al., 2019). Uranium (U)
61 isotopes have played a key role in reconstructing ancient marine redox landscapes,
62 based on the framework that seawater U isotopic compositions are controlled by the
63 | balance between~~of~~ different marine U sinks with distinct isotopic fractionations
64 relative to seawater (Andersen et al., 2017). For instance, extensive euxinia (anoxic
65 | and sulfidic conditions) in open-ocean settings will drive seawater towards very light
66 dissolved U isotopic compositions; whereas more limited euxinic and extensive
67 | oxygenated waters result in isotopically heavier seawater~~with heavy U isotope values~~
68 (*Andersen et al., 2017*). Marine carbonates record seawater U isotope
69 values—providing a seemingly ideal and simple means of tracking global oceanic
70 redox evolution. To date marine carbonates have been the chief geologic archive for
71 reconstructing global seawater U isotope compositions from the Ediacaran to the

72 Cambrian Age 2 (ca. 635–520 Ma) (Wei et al., 2018; Zhang et al., 2018, 2019;
73 Tostevin et al., 2019; Dahl et al., 2019). However, carbonate-hosted U isotopes can be
74 extensively modified during ~~the~~ diagenesis. Early marine diagenesis typically results
75 in more positive carbonate U isotope values, but late-stage alteration of carbonates
76 can result in more negative U isotope values (e.g., Hood et al., 2016, 2018; Chen et al.,
77 2018; Tissot et al., 2018), which can hamper the use of carbonate as a seawater
78 archive. Therefore, there is an obvious motivation to explore other U isotope archives
79 to track global marine redox evolution.

80 Modern reducing sediments generally document higher $\delta^{238}\text{U}$ values, relative to
81 seawater (Weyer et al., 2008; Andersen et al., 2014; Holmden et al., 2015; Abshire et
82 al., 2020; Brüske et al., 2020) because ^{238}U is preferentially reduced and accumulates
83 in reducing sediments via microbially mediated reduction of U (VI) (e.g. Basu et al.,
84 2014; Stirling et al., 2015; Stylo et al., 2015). Observed U isotopic differences
85 between reducing sediments and seawater are sensitive to variations in local
86 depositional environment, including local productivity and sedimentation rates, basin
87 connectivity and bottom-water redox state (Bura-Nakić et al., 2018; Andersen et al.,
88 2018; Brüske et al., 2020; Lau et al., 2020), which adds complexity to precise
89 reconstruction of seawater $\delta^{238}\text{U}$ values. However, given that exposure to reducing
90 conditions will result in higher $\delta^{238}\text{U}$ values in the sediments relative to seawater,
91 reducing sediments can provide a robust maximum estimate for seawater values.
92 Further, integration of $\delta^{238}\text{U}$ analysis of reducing sediments with detailed
93 characterization of the hosting facies can be used to track secular changes in seawater

94 $\delta^{238}\text{U}$ values. In this light, shale- and mudstone-hosted U isotope records can be used
95 to independently test whether the widespread anoxia reconstructed for the Ediacaran
96 and Cambrian, on the basis of carbonate archives, accurately reflects ancient marine
97 conditions.

98 In this study, we report new high-resolution $\delta^{238}\text{U}$ data from two marine
99 siliciclastic successions (Daotuo drill core and Yanjia section) (Fig. 1) in the Yangtze
100 block, South China, which span the terminal Ediacaran to Cambrian Stage 3 (ca.
101 551–515 Ma). We focus on U-enriched ~~silicified shaleshaly-chert~~, shale and mudstone,
102 given that the presence of authigenic U enrichments in these lithologies can provide
103 an archive of seawater $\delta^{238}\text{U}$ values, independent ~~offrom~~ that of shallow carbonates.
104 We measured $\delta^{238}\text{U}$ values from these lithologies, and coupled these to trace element
105 and iron speciation analyses, in order to provide new insights into global seawater
106 $\delta^{238}\text{U}$ evolution and compare these to carbonate $\delta^{238}\text{U}$ records.

107 2. Geological background

108 The Daotuo drill core, collected from Songtao County of northeastern Guizhou
109 Province, South China, is interpreted to record a weakly restricted mid-depth slope
110 environment during the early Cambrian (Wei et al., 2017). The studied Daotuo drill
111 core samples were collected from the upper Liuchapo Formation to the Jiumenchong
112 Formation, which ~~compriseconsist-of~~ black chert, black shale, mudstone and
113 calcareous mudstone (Fig. 1). The upper Liuchapo Formation spans the
114 Ediacaran-Cambrian boundary (ca. 542 Ma), based on ~~a~~-U-Pb zircon

115 | geochronology dating (Chen et al., 2015a). The lower Jiumenchong Formation
116 | contains a polymetallic sulfide-rich layer whose age is 521 ± 5 Ma based on Re-Os
117 | daing (Xu et al., 2011) or younger than 522.7 ± 4.9 Ma based on U-Pb zircon dating
118 | (Wang et al., 2012) ~~offer the~~ correlated strata in other sections from South China. The
119 | Yanjia section is exposed in Chun'an County of Zhejiang Province, South China and
120 | interpreted to have been deposited in a deep basin, relatively well connected to the
121 | open ocean (Wang et al., 2018). The Yanjia section comprises the Piyuancun
122 | Formation and the overlying Hetang Formation, both of which are composed of
123 | organic-rich chert, siliceous shale and black shale. The Piyuancun and Hetang
124 | formations in the Yanjia section can be correlated to the Liuchapo and Jiumenchong
125 | orms in the Daotuo drill core section, respectively (cf. Wang et al., 2018).

126 | Stratigraphic correlations on the Yangtze block are shown in Fig. 1, including
127 | two sections from the inner shelfal and intrashelf basinal settings (Wei et al., 2018).
128 | The studied strata of the Daotuo drill core and Yanjia section are highly condensed in
129 | the Cambrian Fortunian and Stage 2 (ca. 541–521 Ma), ~~which are age equivalent~~
130 | ~~to~~ compared with more expanded –carbonate successions in the Xiaotan and Yanjiahe
131 | sections (cf. Wei et al., 2018; Dahl et al., 2019). Most samples in this study (middle
132 | and upper Jiumenchong and Hetang formations) were deposited during Cambrian Age
133 | 3 (ca. 520–515 Ma), an interval during which deposition of chert, black shale and
134 | siliceous-calcareous mudstones was widespread across the Yangtze block.

135 | **3. Materials and methods**

136 | The studied samples with relatively low Ca concentrations (< 3%) were carefully

137 ~~selected petrographically screened in order to avoid for the effects of~~ any carbonate
138 components and obvious late-stage veins, and then analyzed for U isotopic
139 composition as well as trace element concentration and total organic carbon. HF,
140 HNO₃ and HCl acids were used to fully digest the samples. Trace element
141 concentrations of the studied samples were measured on a Thermo Finnigan Element
142 XR ICP-MS at Yale University and Nanjing University with errors lower than 5%.
143 Uranium isotopes were measured on a Thermo Finnigan Neptune Plus MC-ICP-MS at
144 Yale University following column chromatography using UTEVA resin, using the
145 method described in Wei et al. (2018). Long-term reproducibility was better than 0.07‰
146 (2SD), based on replications of the NOD-A-1 geostandard (-0.61‰ ± 0.05, n = 5) and
147 CRM 112a standard (0.03‰ ± 0.07, n = 42).

148 From among the studied samples for U isotope analyses, representative ones
149 were selected for iron speciation analyses in order to further constrain the local redox
150 conditions. –Iron speciation analyses were ~~completed~~finished at Nanjing University
151 and Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences,
152 following the sequential extraction procedure of Poulton and Canfield (2005) in order
153 to analyze highly reactive Fe in carbonate, oxides and magnetite, and following the
154 Cr-reduction method of Canfield et al. (1986) for extraction of pyrite-associated Fe.
155 Iron concentrations of extracted highly reactive Fe were measured on an atomic
156 absorption spectroscope (AAS) and ICP-OES with errors lower than 5%. The yield of
157 pyrite- Fe was better than 90% based on ~~the~~ repeated analyses of the Chinese
158 GBW07267 pyrite standard. ~~The d~~Details of all ~~the~~ analytical methods are shown in

159 the Supplementary Materials.

160 4. Results and discussion

161 4.1 Uranium isotopes in uppermost Ediacaran through lower Cambrian 162 fine-grained siliciclastic strata: local depositional or global marine redox 163 control?

164 Results of U isotope, Fe speciation, total organic carbon and trace element
165 concentration analyses are shown in Table S1 and Fig. 2. High bulk U/Th ratios
166 (distinctly higher than those of terrestrial detrital materials, $U/Th_{\text{detrital}} = 0.282 \pm 0.102$,
167 2SD) (Cole et al., 2017) and ~~no~~ a lack of any clear ~~covariation~~correlations between
168 bulk U concentrations ($[U]_{\text{bulk}}$), bulk $\delta^{238}\text{U}$ values ($\delta^{238}\text{U}_{\text{bulk}}$) and Al or Th
169 concentrations (Fig. 3~~A, B, C, D~~) suggest only negligible ~~trivial~~ detrital U
170 contribution to our reported U isotope signatures ~~produced from the analyzed samples~~.
171 We therefore interpret measured $\delta^{238}\text{U}$ signatures to record the behavior of
172 predominantly authigenic (seawater-sourced) U deposited in the sediments under
173 potentially anoxic conditions. In order to further disentangle marine authigenic signals
174 from any potential detrital signals in the bulk sample U isotope data, we calculated U
175 concentrations and $\delta^{238}\text{U}$ values of marine authigenic uranium ($[U]_{\text{auth}}$ and $\delta^{238}\text{U}_{\text{auth}}$),
176 by using the equations published in Andersen et al. (2017) with a simple Monte Carlo
177 simulation to evaluate the uncertainties on calculated $\delta^{238}\text{U}_{\text{auth}}$ values (see
178 Supplementary materials for detail). The Daotuo drill core and Yanjia section exhibit
179 consistent trends and a wide range ~~but consistently varying trend~~ of $\delta^{238}\text{U}_{\text{auth}}$ values
180 from -0.63‰ to +0.39‰ and from -0.42‰ to +0.32‰, respectively (Fig. 2). Although

181 [U]_{auth} and $\delta^{238}\text{U}_{\text{auth}}$ of the studied samples vary greatly in the Daotuo and Yanjia
182 sections, no covariation between [U]_{auth} and $\delta^{238}\text{U}_{\text{auth}}$ values show no correlation with
183 Fe contents (Fig. 3E, F) but clear covariation between [U]_{auth} and TOC (total organic
184 carbon) contents (Fig. 4) likely, which likely suggests that U precipitation was
185 dominated by bacterially mediated U reduction, rather than abiotic Fe (II)-mediated U
186 reduction (e.g., Stylo et al., 2015), which highlights the importance of organic
187 substrates on U precipitation in the anoxic sediments (e.g., Tribovillard et al., 2006).

188 Samples from the lowest Jiumenchong and Hetang formations (upper Cambrian
189 Stage 2), show strongly positive $\delta^{238}\text{U}_{\text{auth}}$ values (up to +0.39‰) (Fig. 2), equivalent
190 to or slightly higher than the heaviest reported U isotope compositions of modern
191 euxinic sediments (e.g., as high as that of Black Sea unit II) (Andersen et al., 2014).
192 Although the units with high $\delta^{238}\text{U}_{\text{auth}}$ values in the lowest Jiumenchong and Hetang
193 formations display relatively significantly high [U]_{auth} and total organic carbon (TOC)
194 contents (Figs. 2 and 4), given the lack of significant covariation between $\delta^{238}\text{U}_{\text{auth}}$ and
195 TOC (Fig. 4D), such high $\delta^{238}\text{U}_{\text{auth}}$ values (up to +0.39‰) are unlikely to have been
196 driven primarily by high organic carbon burial fluxes because increased organic carbon
197 delivery within the sediments generally results in rapid U reduction and more
198 quantitative precipitation of U in the sediments, reducing the U isotopic fractionation
199 between sediments and seawater (Andersen et al., 2018; Brüske et al., 2020; Lau et al.,
200 2020). Instead, we suggest that this stratigraphic interval records greater water column
201 or water-sediment interface reduction of U (rather than reduction within the sediment
202 pile) under highly productive conditions, which is consistent with the U isotopic

203 | behavior expected in very highly-productive regions (cf. Rolison et al., 2017; Abshire
204 | et al., 2020; Cheng et al., 2020). Uranium reduction in an unrestricted water column or
205 | at the water–sediment interface may result in a higher effective U isotopic fractionation
206 | between the sediment and ~~coeval~~ ~~concurrent~~ seawater (Rolison et al., 2017; Andersen et
207 | al., 2017; Brüske et al., 2020; Abshire et al., 2020). Nonetheless, even if the U isotope
208 | offset between sediment and seawater $\delta^{238}\text{U}$ ~~was~~ ~~is~~ large, comparable to the largest
209 | offsets ($\sim 0.8\%$) observed in modern anoxic depositional systems (Rolison et al.,
210 | 2017; Brüske et al., 2020), high $\delta^{238}\text{U}_{\text{auth}}$ values (up to $+0.39\%$) recorded here likely
211 | reflect near-modern seawater $\delta^{238}\text{U}$ values. In this view, high seawater $\delta^{238}\text{U}$ values in
212 | this interval ~~indicates~~ ~~suggest~~ a relatively limited extent of anoxic seawater during late
213 | Cambrian Age 2, which is consistent with previously published Mo isotope records
214 | (Chen et al., 2015b).

215 | In contrast, the Liuchapo and upper Piyuancun formations and the middle to
216 | upper Jiumenchong and Hetang formations are marked by low $\delta^{238}\text{U}_{\text{auth}}$ values ($<$
217 | -0.6%) that are notably lower than that of modern seawater (Fig. 2). In fact, these are
218 | the most negative shale U isotopic values (as low as -0.63%) that have ever been
219 | reported (cf. Wang et al., 2018). These values likely reflect nearly complete U
220 | reduction (which can occur in an isolated basin or in porewaters beneath suboxic
221 | bottom water). With near quantitative capture of a U reservoir, $\delta^{238}\text{U}_{\text{auth}}$ values of
222 | sediments can approach that of seawater (Noordmann et al., 2015; Andersen et al.,
223 | 2016, 2018; Bura-Nakić et al., 2018). However, even if there is no appreciable U
224 | isotopic difference between sediments and seawater, the remarkably negative $\delta^{238}\text{U}_{\text{auth}}$

225 values in the Liuchapo and upper Piyuancun formations and middle to upper
226 | Jiumenchong and Hetang formations imply remarkablymarkedly low seawater $\delta^{238}\text{U}$
227 values (as low as -0.63%) across the Ediacaran-Cambrian boundary and during
228 Cambrian Age 3, suggesting widespread marine anoxia during these intervals.

229 To further determine local depositional conditions and thus constrain U isotopic
230 differences between open seawater and the local sediments, we conducted iron
231 speciation analyses ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ and $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$) and Mo, U enrichment factors (Mo_{EF}
232 and U_{EF}) (see Supplementary materials for calculations). Using the standard iron
233 speciation framework (Poulton and Canfield, 2011), essentially all the samples
234 included in this study were deposited under anoxic—but not persistently and strongly
235 | sulfidic—bottom water (Fig. 54A). We do not observe any systematic relationships
236 | between $\delta^{238}\text{U}_{\text{auth}}$ and $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$, $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ (Fig. 6S), which suggests that redox
237 conditions of local bottom water may have not been the dominant factor controlling
238 $\delta^{238}\text{U}_{\text{auth}}$ values of the studied samples. Covariation of Mo_{EF} and U_{EF} is used to further
239 evaluate the depositional environment of the samples in this study and to compare
240 these with modern low-oxygen marine sedimentary systems (cf. Algeo and
241 | Tribovillard, 2009; Tribovillard et al., 2012). As shown in Fig. 54B, most of the
242 samples in this study fall within the iron speciation field characteristic of deposition
243 under anoxic conditions and show a $\text{Mo}_{\text{EF}}-\text{U}_{\text{EF}}$ trend analogous to that of modern
244 open-ocean settings (cf. Algeo and Tribovillard, 2009; Tribovillard et al., 2012),
245 which with the standard interpretation would suggest that the Yangtze continental
246 margin was likely well-connected to the open ocean during the early Cambrian. A few

247 samples with relatively low Mo_{EF} and U_{EF} values have significantly low $\delta^{238}U_{auth}$
248 values, potentially representing a locally suboxic ~~local~~ depositional environment
249 with less U isotopic fractionation between the sediments and seawater. Collectively,
250 these observations—Fe speciation and Mo_{EF} – U_{EF} covariation—imply that, during the
251 early Cambrian, local bottom waters in these regions were well connected to the open
252 ~~ocean waters~~ and experienced relatively prolonged intervals of strong anoxia. Taken
253 together, we suggest that swings in $\delta^{238}U_{auth}$ values from the Daotuo drill core and
254 Yanjia section ~~were~~ not solely controlled by local ~~variability~~ variation in basin
255 restriction, organic carbon delivery or bottom water redox conditions. Highly
256 consistent $\delta^{238}U_{auth}$ variations in these two sections, in part, reflect frequent
257 fluctuations in seawater $\delta^{238}U$ values. ~~Most importantly~~ Foremost, the anomalously
258 positive $\delta^{238}U_{auth}$ ~~values of~~ values in upper Cambrian Stage 2 and negative $\delta^{238}U_{auth}$ values
259 ~~of~~ Stage 3 strata provide evidence, independent of carbonate $\delta^{238}U$ records, for
260 ~~substantial intense and rapid~~ oscillations ~~in~~ of oceanic redox states throughout the
261 Cambrian explosion.

262 **4.2 Reconstruction of seawater $\delta^{238}U$ from the late Ediacaran to early Cambrian** 263 **via siliciclastic archives**

264 Based on the above Fe speciation and Mo_{EF} – U_{EF} analyses, we reconstruct
265 temporal changes in seawater U isotopic compositions ($\delta^{238}U_{SW}$, Fig. 76C) from the
266 reducing sedimentary records of this study by using +0.8‰, +0.6‰, +0.15‰,
267 respectively, as the U isotopic offsets for 1) authigenic U reduction within the

268 high-productive water column or water-sediment interface with efficient
269 replenishment of dissolved U (Rolison et al., 2017; Brüske et al., 2020); 2) within
270 sulfidic sediments of an unrestricted basin (Holmden et al., 2015; Andersen et al.,
271 | 2018) and 3) within suboxic sediments— (Weyer et al., 2008; Andersen et al., 2016).
272 | Although U isotopic behaviors in ~~the~~ reducing sediments may be more complex,
273 | simplified estimation of U isotopic offsets under different local conditions can provide
274 | insights into secular changes in ancient $\delta^{238}\text{U}_{\text{SW}}$ values. Despite the relatively
275 | low-resolution nature of upper Ediacaran and Cambrian Fortunian $\delta^{238}\text{U}_{\text{auth}}$ data (e.g.,
276 | three points from potentially suboxic samples for Fortunian excursion P1 in Fig. 7C)
277 | and the errors inherent to estimating an effective U isotopic fractionation, secular
278 | changes in $\delta^{238}\text{U}_{\text{SW}}$ reconstructed from siliciclastic rocks are strikingly consistent with
279 | correlative carbonate $\delta^{238}\text{U}$ profiles (Fig. 7A). This supports the interpretation that
280 | changes in $\delta^{238}\text{U}_{\text{auth}}$ mainly reflect global oceanic redox changes. Further, compared to
281 | previous studies of carbonate-hosted U isotopic signatures (Fig. 7A), the new
282 | $\delta^{238}\text{U}_{\text{SW}}$ curve documented in siliciclastic strata provides a higher-resolution record of
283 | global oceanic redox states through Cambrian Age 3, and suggests that this critical
284 | interval of the Cambrian explosion is marked by large swings in marine redox states.

285 **4.3 Implications for co-evolution of marine environments and early metazoans**

286 We provide estimates of late Ediacaran to early Cambrian (ca. 551 Ma–515 Ma)
287 seawater $\delta^{238}\text{U}$ records from fine-grained siliciclastic rocks that closely match
288 | previous estimates from carbonates (Fig. 7). This provides compelling evidence that
289 | the early Cambrian was indeed marked by frequent rapid variations in seawater $\delta^{238}\text{U}$

290 (negative excursion N1–N3 and positive excursion P1–P3 in Fig. 76). These swings
291 demonstrate that there were largescale fluctuations in the marine redox landscape
292 (with the U mass balance being tied foremost to the areal extent of anoxic conditions).

293 The frequently fluctuating redox states of the early Cambrian ocean are likely linked
294 to effects of dynamic nutrient supply, shallow marine productivity and ocean
295 ventilation in the ocean with relatively lower baseline oxygenation level than the
296 modern ocean (cf. Wang et al., 2018; He et al., 2019; Dahl et al., 2019; Wei et al.,
297 2020). Further studies are needed to better constrain the triggers for the dramatic
298 changes in marine redox states during this period. The synchronicity of this dynamic
299 redox variation with animal evolutionary^{ry} clades, increased physiological and
300 ecological complexity and expansion into a wider range of benthic habitats and water
301 depths may, moreover, not be coincidental. In fact, this concurrence provides further
302 empirical evidence in favor of recent proposals that habitat fragmentation and
303 ecological restructuring mediated by redox instability may have facilitated higher
304 rates of generation of evolutionary novelties and thus enhanced biological innovation
305 and turnover—thus serving as a spur, rather than an impediment, to diversification
306 among animal lineages over this interval (Reinhard et al., 2016; Wood and Erwin,
307 2018). In this light, rather than being an anomalous episode in Earth’s history, the
308 Ediacaran–Cambrian protracted emergence and subsequent rapid radiations of
309 complex animal life (and Ediacaran–Ordovician emergence of modern-style
310 ecological strategies and ecosystem structure) against a backdrop of pronounced
311 environmental instability (Droser et al., 2017; Tarhan et a., 2018; Servais and Harper,

312 2018; Wood et al., 2019), broadly resembles patterns of emergence and turnover
313 characteristic of Sepkoskian Phanerozoic Evolutionary Faunas (e.g., Tarhan et al.,
314 2018).

315 **5. Conclusions**

316 New high-resolution uranium isotope data from two upper Ediacaran through
317 Cambrian Stage 3 siliciclastic sections in South China are reported in this study. Both
318 of the studied sections show mutually consistent, ~~ly~~ large swings in authigenic $\delta^{238}\text{U}$
319 values. Given that local depositional conditions ~~did~~~~may~~~~have~~ not dominated
320 authigenic $\delta^{238}\text{U}$ values of the studied samples, we interpret much of this variability to
321 be driven by secular changes in seawater $\delta^{238}\text{U}$ values. Notably high authigenic $\delta^{238}\text{U}$
322 values in upper Cambrian Stage 2 and lowest Stage 3 suggest that host sediments
323 were deposited in and ocean with limited anoxic seafloor area~~anoxia~~, whereas
324 anomalously negative authigenic $\delta^{238}\text{U}$ values in the terminal Ediacaran and
325 Cambrian Stage 3 are indicative of extensive deep-marine anoxia. Paired $\delta^{238}\text{U}$
326 records from marine carbonates (Wei et al., 2018; Zhang et al., 2018; Tostevin et al.,
327 2019; Dahl et al., 2019) and siliciclastic strata strengthens the case that anomalously
328 high $\delta^{238}\text{U}$ variability (e.g., Wei et al., 2018; Dahl et al., 2019) is ~~indeed~~ tied to
329 episodic~~the frequent~~ swings in global marine redox states from the late Ediacaran
330 through the early Cambrian (ca. 551 Ma–510 Ma), rather than~~instead of~~ diagenetic
331 overprinting. This bolsters the hypothesis that the diversification of early animals
332 during the Cambrian explosion occurred against a backdrop of (and may even have
333 been mediated by) highly spatiotemporally variable marine redox conditions.

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344 **References**

- 345 Abshire, M.L., Romaniello, S.J., Kuzminov, A.M., Cofrancesco, J., Severmann, S.,
346 Riedinger, N., 2020. Uranium isotopes as a proxy for primary depositional redox
347 conditions in organic-rich marine systems. *Earth and Planetary Science Letters*
348 529, 115878.
- 349 Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic
350 systems based on molybdenum–uranium covariation. *Chemical Geology* 268,
351 211-225.
- 352 Andersen, M.B., Romaniello, S., Vance, D., Little, S.H., Herdman, R., Lyons, T.W.,
353 2014. A modern framework for the interpretation of $^{238}\text{U}/^{235}\text{U}$ in studies of
354 ancient ocean redox. *Earth and Planetary Science Letters* 400, 184-194.
- 355 Andersen, M.B., Stirling, C. H., Weyer, S., 2017. Uranium Isotope Fractionation.

356 Reviews in Mineralogy and Geochemistry 82, 799-850.

357 Andersen, M.B., Vance, D., Morford, J.L., Bura-Nakić, E., Breitenbach, S.F.M., Och,
358 L., 2016. Closing in on the marine $^{238}\text{U}/^{235}\text{U}$ budget. *Chemical Geology* 420,
359 11-22.

360 Andersen, M.B., Matthews, A., Vance, D., Bar-Matthews, M., Archer, C., de Souza,
361 G.F., 2018. A 10-fold decline in the deep Eastern Mediterranean thermohaline
362 overturning circulation during the last interglacial period. *Earth and Planetary*
363 *Science Letters* 503, 58-67.

364 Basu, A., Sanford, R. A., Johnson, T. M., Lundstrom, C. C., Loffler, F. E., 2014.
365 Uranium isotopic fractionation factors during U(VI) reduction by bacterial
366 isolates. *Geochimica et Cosmochimica Acta* 136, 100-113.

367 Brüske, A., Weyer, S., Zhao, M.Y., Planavsky, N.J., Wegwerth, A., Neubert, N.,
368 Dellwig, O., Lau, K.V., Lyons, T.W., 2020. Correlated molybdenum and uranium
369 isotope signatures in modern anoxic sediments: Implications for their use as
370 paleo-redox proxy. *Geochimica et Cosmochimica Acta* 270, 449-474.

371 Bura-Nakić, E., Andersen, M.B., Archer, C., de Souza, G.F., Marguš, M., Vance, D.,
372 2018. Coupled Mo-U abundances and isotopes in a small marine euxinic basin:
373 Constraints on processes in euxinic basins. *Geochimica et Cosmochimica Acta*
374 222, 212-229.

375 Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The
376 use of chromium reduction in the analysis of reduced inorganic sulfur in
377 sediments and shales. *Chemical Geology* 54, 149-155.

378 Chen, D., Zhou, X., Fu, Y., Wang, J., Yan, D., 2015a. New U-Pb zircon ages of the
379 Ediacaran-Cambrian boundary strata in South China. *Terra Nova* 27, 62-68.

380 Chen, X., Ling, H.F., Vance, D., Shields-Zhou, G.A., Zhu, M., Poulton, S.W., Och,
381 L.M., Jiang, S.Y., Li, D., Cremonese, L., Archer, C., 2015b. Rise to modern
382 levels of ocean oxygenation coincided with the Cambrian radiation of animals.
383 *Nat Commun* 6, 7142.

384 Chen, X., Romaniello, S.J., Herrmann, A.D., Hardisty, D., Gill, B.C., Anbar, A.D.,
385 2018. Diagenetic effects on uranium isotope fractionation in carbonate sediments
386 from the Bahamas. *Geochimica et Cosmochimica Acta* 237, 294-311.

387 Cheng, M., Li, C., Jin, C., Wang, H., Algeo, T.J., Lyons, T.W., Zhang, F., Anbar, A.,
388 2020. Evidence for high organic carbon export to the early Cambrian seafloor.
389 *Geochimica et Cosmochimica Acta*. In press.

390 Cole, D.B., Zhang, S., Planavsky, N.J., 2017. A new estimate of detrital
391 redox-sensitive metal concentrations and variability in fluxes to marine
392 sediments. *Geochimica Et Cosmochimica Acta* 215, 337-353.

393 Dahl, T.W., Connelly, J.N., Li, D., Kouchinsky, A., Gill, B.C., Porter, S., Maloof, A.C.,
394 Bizzarro, M., 2019. Atmosphere-ocean oxygen and productivity dynamics during
395 early animal radiations. *Proc. Natl. Acad. Sci. USA* 116, 19352-19361.

396 Droser, M.L., Tarhan, L.G., Gehling, J.G., 2017. The Rise of Animals in a Changing
397 Environment: Global Ecological Innovation in the Late Ediacaran. *Annual*
398 *Review of Earth and Planetary Sciences* 45, 593-617.

399 | [He, T., Zhu, M., Mills, B.J.W., Wynn, P.M., Zhuravlev, A.Y., Tostevin, R., Pogge von](#)

400 [Strandmann, P.A.E., Yang, A., Poulton, S.W., Shields, G.A., 2019. Possible links](#)
401 [between extreme oxygen perturbations and the Cambrian radiation of animals.](#)
402 [Nature Geoscience 12, 468-474.](#)

403 Holmden, C., Amini, M., Francois, R., 2015. Uranium isotope fractionation in
404 Saanich Inlet: A modern analog study of a paleoredox tracer. *Geochimica et*
405 *Cosmochimica Acta* 153, 202-215.

406 Hood, A.v.S., Planavsky, N.J., Wallace, M.W., Wang, X., Bellefroid, E.J., Gueguen, B.,
407 Cole, D.B., 2016. Integrated geochemical-petrographic insights from
408 component-selective $\delta^{238}\text{U}$ of Cryogenian marine carbonates. *Geology* 44,
409 935-938.

410 Hood, A.v.S., Planavsky, N.J., Wallace, M.W., Wang, X., 2018. The effects of
411 diagenesis on geochemical paleoredox proxies in sedimentary carbonates.
412 *Geochimica et Cosmochimica Acta* 232, 265-287.

413 Lau, K.V., Lyons, T.W., Maher, K., 2020. Uranium reduction and isotopic
414 fractionation in reducing sediments: Insights from reactive transport modeling.
415 *Geochimica et Cosmochimica Acta*. In press.

416 Lyons, T.W., Reinhard, C.T., Planavsky, N.J., 2014. The rise of oxygen in Earth's
417 early ocean and atmosphere. *Nature* 506, 307-315.

418 Noordmann, J., Weyer, S., Montoya-Pino, C., Dellwig, O., Neubert, N., Eckert, S.,
419 Paetzel, M., Böttcher, M.E., 2015. Uranium and molybdenum isotope
420 systematics in modern euxinic basins: Case studies from the central Baltic Sea
421 and the Kyllaren fjord (Norway). *Chemical Geology* 396, 182-195.

422 Och, L.M., Shields-Zhou, G.A., 2012. The Neoproterozoic oxygenation event:
423 Environmental perturbations and biogeochemical cycling. *Earth-Science*
424 *Reviews* 110, 26-57.

425 Poulton, S., Canfield, D., 2005. Development of a sequential extraction procedure for
426 iron: implications for iron partitioning in continentally derived particulates.
427 *Chemical Geology* 214, 209-221.

428 Poulton, S.W., Canfield, D.E., 2011. Ferruginous Conditions: A Dominant Feature of
429 the Ocean through Earth's History. *Elements* 7, 107-112.

430 Reinhard, C.T., Planavsky, N.J., Olson, S.L., Lyons, T.W., Erwin, D.H., 2016. Earth's
431 oxygen cycle and the evolution of animal life. *Proc. Natl. Acad. Sci. USA* 113,
432 8933-8938.

433 Rolison, J.M., Stirling, C.H., Middag, R., Rijkenberg, M.J.A., 2017. Uranium stable
434 isotope fractionation in the Black Sea: Modern calibration of the $^{238}\text{U}/^{235}\text{U}$
435 paleo-redox proxy. *Geochimica et Cosmochimica Acta* 203, 69-88.

436 Servais, T., Harper, D.A.T., 2018. The Great Ordovician Biodiversification Event
437 (GOBE): definition, concept and duration. *Lethaia* 51, 151-164.

438 Sperling, E.A., Frieder, C.A., Raman, A.V., Girguis, P.R., Levin, L.A., Knoll, A.H.,
439 2013. Oxygen, ecology, and the Cambrian radiation of animals. *Proc. Natl. Acad.*
440 *Sci. USA* 110, 13446-13451.

441 Sperling, E.A., Knoll, A.H., Girguis, P.R., 2015. The Ecological Physiology of Earth's
442 Second Oxygen Revolution. *Annual Review of Ecology, Evolution, and*
443 *Systematics* 46, 215-235.

444 Stirling, C.H., Andersen, M.B., Warthmann, R., Halliday, A.N., 2015. Isotope
445 fractionation of ^{238}U and ^{235}U during biologically-mediated uranium reduction.
446 *Geochimica et Cosmochimica Acta* 163, 200-218.

447 Stylo, M., Neubert, N., Wang, Y., Monga, N., Romaniello, S.J., Weyer, S.,
448 Bernier-Latmani, R., 2015. Uranium isotopes fingerprint biotic reduction. *Proc.*
449 *Natl. Acad. Sci. USA* 112, 5619-5624.

450 Tarhan, L.G., Droser, M.L., Cole, D.B., Gehling, J.G., 2018. Ecological Expansion
451 and Extinction in the Late Ediacaran: Weighing the Evidence for Environmental
452 and Biotic Drivers. *Integr. Comp. Biol.* 58, 688-702.

453 Tissot, F.L.H., Chen, C., Go, B.M., Naziemiec, M., Healy, G., Bekker, A., Swart, P.K.,
454 Dauphas, N., 2018. Controls of eustasy and diagenesis on the $^{238}\text{U}/^{235}\text{U}$ of
455 carbonates and evolution of the seawater ($^{234}\text{U}/^{238}\text{U}$) during the last 1.4 Myr.
456 *Geochimica et Cosmochimica Acta* 242, 233-265.

457 Tostevin, R., Clarkson, M.O., Gangl, S., Shields, G.A., Wood, R.A., Bowyer, F.,
458 Penny, A.M., Stirling, C.H., 2019. Uranium isotope evidence for an expansion of
459 anoxia in terminal Ediacaran oceans. *Earth and Planetary Science Letters* 506,
460 104-112.

461 Tribovillard, N., Algeo, T.J., Baudin, F., Riboulleau, A., 2012. Analysis of marine
462 environmental conditions based on molybdenum–uranium
463 covariation—Applications to Mesozoic paleoceanography. *Chemical Geology*
464 324-325, 46-58.

465 | [Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as](#)

466 [paleoredox and paleoproductivity proxies: An update. Chemical Geology 232,](#)
467 [12-32.](#)

468 Wang, D., Ling, H.-F., Struck, U., Zhu, X.-K., Zhu, M., He, T., Yang, B., Gamper, A.,
469 Shields, G. A., 2018a. Coupling of ocean redox and animal evolution during the
470 Ediacaran-Cambrian transition. *Nature Communications* 9, 2575.

471 Wang, X.L., Planavsky, N.J., Hofmann, A., Saupe, E.E., De Corte, B.P., Philippot, P.,
472 LaLonde, S.V., Jemison, N.E., Zou, H.J., Ossa, F.O., Rybacki, K., Alfimova, N.,
473 Larson, M.J., Tsikos, H., Fralick, P.W., Johnson, T.M., Knudsen, A.C., Reinhard,
474 C.T., Konhauser, K.O., 2018b. A Mesoarchean shift in uranium isotope
475 systematics. *Geochimica Et Cosmochimica Acta* 238, 438-452.

476 Wang, X., Shi, X., Jiang, G., Zhang, W., 2012. New U–Pb age from the basal
477 Niutitang Formation in South China: Implications for diachronous development
478 and condensation of stratigraphic units across the Yangtze platform at the
479 Ediacaran–Cambrian transition. *Journal of Asian Earth Sciences* 48, 1-8.

480 Wei, G.-Y., Ling, H.-F., Li, D., Wei, W., Wang, D., Chen, X., Zhu, X.-K., Zhang, F.-F.,
481 Yan, B., 2017. Marine redox evolution in the early Cambrian Yangtze shelf
482 margin area: evidence from trace elements, nitrogen and sulphur isotopes.
483 *Geological Magazine* 154, 1344-1359.

484 Wei, G.-Y., Planavsky, N.J., Tarhan, L.G., Chen, X., Wei, W., Li, D., Ling, H.-F., 2018.
485 Marine redox fluctuation as a potential trigger for the Cambrian explosion.
486 *Geology* 46, 587-590.

487 [Wei, G.-Y., Wei, W., Wang, D., Li, T., Yang, X., Shields, G.A., Zhang, F., Li, G., Chen,](#)

488 [T., Yang, T., Ling, H.-F., 2020. Enhanced chemical weathering triggered an](#)
489 [expansion of euxinic seawater in the aftermath of the Sturtian glaciation. Earth](#)
490 [and Planetary Science Letters 539, 116244.](#)

491 Weyer, S., Anbar, A.D., Gerdes, A., Gordon, G.W., Algeo, T.J., Boyle, E.A., 2008.
492 Natural fractionation of $^{238}\text{U}/^{235}\text{U}$. *Geochimica et Cosmochimica Acta* 72,
493 345-359.

494 Wood, R., Bowyer, F., Penny, A., Poulton, S.W., 2018. Did anoxia terminate
495 Ediacaran benthic communities? Evidence from early diagenesis. *Precambrian*
496 *Research* 313, 134-147.

497 Wood, R., Erwin, D.H., 2018. Innovation not recovery: dynamic redox promotes
498 metazoan radiations. *Biol. Rev. Camb. Philos. Soc.* 93, 863-873.

499 Wood, R., Liu, A.G., Bowyer, F., Wilby, P.R., Dunn, F.S., Kenchington, C.G., Cuthill,
500 J.F.H., Mitchell, E.G., Penny, A., 2019. Integrated records of environmental
501 change and evolution challenge the Cambrian Explosion. *Nat. Ecol. Evol.* 3,
502 528-538.

503 Xu, L., Lehmann, B., Mao, J., Qu, W., Du, A., 2011. Re-Os Age of Polymetallic
504 Ni-Mo-PGE-Au Mineralization in Early Cambrian Black Shales of South
505 China--A Reassessment. *Economic Geology* 106, 511-522.

506 Zhang, F., Xiao, S., Kendall, B., Romaniello, S.J., Cui, H., Meyer, M., Gilleaudeau,
507 G.J., Kaufman, A.J., Anbar, A.D., 2018. Extensive marine anoxia during the
508 terminal Ediacaran Period. *Science Advances* 4, eaan8983.

509 Zhang, F., Xiao, S., Romaniello, S.J., Hardisty, D., Li, C., Melezhik, V., Pokrovsky, B.,

510 Cheng, M., Shi, W., Lenton, T.M., Anbar, A.D., 2019. Global marine redox
511 changes drove the rise and fall of the Ediacara biota. *Geobiology* 17, 594-610.

512

513 **Figure captions**

514 **Figure 1.** Stratigraphic columns of the Daotuo drill core and Yanjia sections, and their
515 correlations to inner shelf Xiaotan section and Gaojiaxi–Yanjiahe section in South China (cf.
516 Wei et al., 2018). The shaded areas represent the correlative stratigraphic units of these
517 sections for the Ediacaran (blue), Cambrian Fortunian and Stage 2 (green) and Stage 3
518 (yellow). The red line represents a Ni-Mo polymetallic layer with an age of 521 ± 5 Ma
519 (Re-Os dating from Xu et al., 2011) or $< 522.7 \pm 4.9$ Ma (U-Pb zircon dating from Wang et al.,
520 2012).

521 **Figure 2.** Uranium isotope ($\delta^{238}\text{U}_{\text{auth}}$) values, iron speciation, U_{auth} concentrations and total
522 organic carbon (TOC) contents of the upper Ediacaran to lower Cambrian Daotuo drill core
523 and Yanjia section. Uranium isotope values are presented as $\delta^{238}\text{U}_{\text{auth}}$ for authigenic uranium
524 in bulk samples. $\delta^{238}\text{U}_{\text{auth}}$ calculation are shown in Supplementary materials. The error bar
525 represents an overall uncertainty (2SD) of calculated $\delta^{238}\text{U}_{\text{auth}}$ for each sample, using a Monte
526 Carlo approach. The shaded vertical bars are estimated average $\delta^{238}\text{U}$ ranges of suboxic and
527 euxinic sediments (Andersen et al., 2017).

528 **Figure 3.** Cross-plots of (A) bulk U concentration vs. Al concentration, (B) bulk $\delta^{238}\text{U}$ vs. Al
529 concentration, (C) bulk U concentration vs. Th concentration, (D) bulk $\delta^{238}\text{U}$ vs. Th
530 concentration, ~~(E) authigenic U concentration vs. Fe concentration, (F) authigenic $\delta^{238}\text{U}$ vs.~~
531 ~~Fe concentration~~ for samples from the Daotuo drill core and Yanjia section. R^2 represents the

532 coefficient of determination of the covariation.
533 Figure 4. Cross plots of (A) authigenic U concentration vs. Fe concentration, (B) authigenic
534 $\delta^{238}\text{U}$ vs. Fe concentration, (C) authigenic U concentration vs. TOC concentration, (D)
535 authigenic $\delta^{238}\text{U}$ vs. TOC concentration for samples from the Daotuo drill core and Yanjia
536 section. R^2 represents the coefficient of determination of the covariation.

537 **Figure 54.** (A) $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ vs. $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ for the samples from the Daotuo drill core and Yanjia
538 section analyzed in this study. The divisions between oxic and anoxic conditions ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} =$
539 $0.22\text{--}0.38$) and between ferruginous and euxinic conditions ($\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}} = 0.7\text{--}0.8$) are derived
540 from Poulton and Canfield (2011). (B) Cross-plots of Mo_{EF} vs. U_{EF} for the samples from the
541 Daotuo drill core and Yanjia section in this study as a proxy for local marine sedimentary
542 environment. The shaded zones for different sedimentary environment of the modern ocean
543 are modified after Algeo and Tribovillard (2009) and Tribovillard et al. (2012). Particulate
544 shuttle zone: the transport of Mo within the water column by Fe-Mn-oxyhydroxide
545 particulates (e.g., as in the Cariaco Basin); Open marine zone: benthic redox variations in
546 modern open-ocean systems; Strongly restricted basin: sedimentary basin weakly connected
547 to the open-ocean (e.g., as in the Black Sea).

548 **Figure 65.** Cross-plots of (A) authigenic $\delta^{238}\text{U}$ vs. $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$, (B) authigenic $\delta^{238}\text{U}$ vs.
549 $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ for the samples in the Daotuo drill core and Yanjia section.

550 **Figure 76.** (A)–(B) Secular changes in U isotopic compositions of carbonates (data from Wei
551 et al., 2018; Zhang et al., 2018; Tostevin et al., 2019; Dahl et al., 2019) and siliciclastic rocks
552 from the late Ediacaran to early Cambrian. (C) Calculated $\delta^{238}\text{U}_{\text{SW}}$ values derived from
553 $\delta^{238}\text{U}_{\text{auth}}$ records in this study. The solid curves are LOWESS smoothing fits for U isotope

554 data. Based on TOC, $\text{Mo}_{\text{EF}}-\text{U}_{\text{EF}}$ and Fe speciation analyses, U isotopic differences between
555 reducing sediment and seawater are estimated to be +0.8‰ for organic-rich anoxic or sulfidic
556 samples with TOC > 5 wt% and Mo_{EF} and $\text{U}_{\text{EF}} > 20$ (purple circles); +0.6‰ for anoxic
557 samples with TOC < 5wt%, Mo_{EF} and $\text{U}_{\text{EF}} > 10$ (orange circles); and +0.15‰ for potentially
558 suboxic samples with Mo_{EF} and $\text{U}_{\text{EF}} < 10$ (gray circles). The shaded vertical bars are
559 estimated average $\delta^{238}\text{U}$ ranges of modern non-skeletal carbonates, suboxic sediments and
560 euxinic sediments (Andersen et al., 2017). N1–N3 and P1–P3 represent negative and positive
561 U isotopic excursions from the late Ediacaran through the early Cambrian.

Highlights

- High-resolution U isotope data from early Cambrian siliciclastic sections
- Global marine redox changes dominate U isotopes of the studied samples
- Frequent marine redox fluctuations likely trigger the early animal innovation

1 **Highly dynamic marine redox states through the Cambrian explosion**

2 **highlighted by authigenic $\delta^{238}\text{U}$ records**

3 Guang-Yi Wei^{1,2*}, Noah J. Planavsky², Lidya G. Tarhan², Tianchen He³, Dan Wang⁴,

4 Graham A. Shields⁵, Wei Wei⁶, Hong-Fei Ling^{1*}

5 ¹*State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and*
6 *Engineering, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, China*

7 ²*Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA*

8 ³*School of Earth and Environment, University of Leeds, Leeds, U.K.*

9 ⁴*School of Geographic Science, Nantong University, Nantong 226019, China*

10 ⁵*Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT,*
11 *U.K.*

12 ⁶*CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and*
13 *Space Sciences, University of Science and Technology of China, Anhui 230026, China*

14

15 *Guang-Yi Wei (guangyiwei@nju.edu.cn); Hong-Fei Ling (hfling@nju.edu.cn)

16

17 **Abstract**

18 The history of oceanic oxygenation from the late Neoproterozoic to the early
19 Cambrian is currently debated, making it difficult to gauge whether, and to what
20 extent environmental triggers played a role shaping the trajectory of metazoan
21 diversification. Uranium isotope ($\delta^{238}\text{U}$) records from carbonates have recently been
22 used to argue for significant swings in the global marine redox states from the late
23 Neoproterozoic to the early Cambrian. However, geochemical signatures in
24 carbonates—the U isotope archive most commonly employed to argue for redox
25 shifts—are susceptible to diagenetic alteration and have variable offsets from
26 seawater values. Therefore, there is an impetus to reconstruct seawater U isotopic
27 evolution using another sedimentary archive, in order to crosscheck that these
28 excursions can indeed be linked to global shifts in marine redox landscape. Here we

29 report new U isotope data from two fine-grained siliciclastic upper Ediacaran to lower
30 Cambrian (ca. 551 Ma–515 Ma) successions in South China. We find large $\delta^{238}\text{U}$
31 swings between -0.63‰ and +0.39‰ for calculated values of authigenic U in the
32 siliciclastic rocks, consistent with correlative records from the carbonates. The
33 replication of these patterns in both carbonate and siliciclastic units provides
34 confirmatory evidence that the early Cambrian seawater was characterized by highly
35 variable U isotope compositions. These new $\delta^{238}\text{U}$ data also provide higher-resolution
36 records of global oceanic redox during Cambrian Age 3, coeval with a critical interval
37 of the Cambrian explosion. These $\delta^{238}\text{U}$ data bolster the case that the
38 Ediacaran-Cambrian transition experienced massive swings in marine redox state,
39 providing a dynamic environmental backdrop for and potentially even a key driver of
40 the emergence and radiation of metazoans.

41 **Keywords**

42 uranium isotopes; siliciclastic strata; early Cambrian; marine redox dynamics; animal
43 innovations

44 **1. Introduction**

45 There has been longstanding debate over whether the Ediacaran–Cambrian
46 emergence and diversification of metazoans coincided with progressive oxidation of
47 the ocean-atmosphere system and, if so, to what extent this environmental transition
48 may have directly influenced the trajectory or pace of metazoan evolution (Och and
49 Shields-Zhou, 2012; Lyons et al., 2014; Sperling et al., 2013, 2015). In contrast to the

50 standard view of a largely unidirectional redox transition, several recent studies have
51 suggested that, during the interval spanning the Ediacaran to the early Cambrian,
52 pulses of widespread marine anoxia were common and recurrent (Wei et al., 2018;
53 Wood et al., 2018; Zhang et al., 2018, 2019; Tostevin et al., 2019; Dahl et al., 2019).
54 Building upon this emerging record of environmental variability, it has been
55 suggested that temporally and spatially dynamic environmental conditions, rather than
56 stymying the emergence of complex life, actually spurred the development and
57 dissemination of biotic novelties, and thus the rapid diversification, turnover and
58 ecosystem restructuring characteristic of this interval (Wei et al., 2018; Wood and
59 Erwin, 2018; Wood et al., 2019). Uranium (U) isotopes have played a key role in
60 reconstructing ancient marine redox landscapes, based on the framework that
61 seawater U isotopic compositions are controlled by the balance between different
62 marine U sinks with distinct isotopic fractionations relative to seawater (Andersen et
63 al., 2017). For instance, extensive euxinia (anoxic and sulfidic conditions) in
64 open-ocean settings will drive seawater towards very light dissolved U isotopic
65 compositions, whereas more limited euxinic and extensive oxygenated waters result
66 in isotopically heavier seawater (Andersen et al., 2017). Marine carbonates record
67 seawater U isotope values—providing a seemingly ideal and simple means of tracking
68 global oceanic redox evolution. To date marine carbonates have been the chief
69 geologic archive for reconstructing global seawater U isotope compositions from the
70 Ediacaran to the Cambrian Age 2 (ca. 635–520 Ma) (Wei et al., 2018; Zhang et al.,
71 2018, 2019; Tostevin et al., 2019; Dahl et al., 2019). However, carbonate-hosted U

72 isotopes can be extensively modified during diagenesis. Early marine diagenesis
73 typically results in more positive carbonate U isotope values, but late-stage alteration
74 of carbonates can result in more negative U isotope values (e.g., Hood et al., 2016,
75 2018; Chen et al., 2018; Tissot et al., 2018), which can hamper the use of carbonate as
76 a seawater archive. Therefore, there is an obvious motivation to explore other U
77 isotope archives to track global marine redox evolution.

78 Modern reducing sediments generally document higher $\delta^{238}\text{U}$ values, relative to
79 seawater (Weyer et al., 2008; Andersen et al., 2014; Holmden et al., 2015; Abshire et
80 al., 2020; Brüske et al., 2020) because ^{238}U is preferentially reduced and accumulates
81 in reducing sediments via microbially mediated reduction of U (VI) (e.g. Basu et al.,
82 2014; Stirling et al., 2015; Stylo et al., 2015). Observed U isotopic differences
83 between reducing sediments and seawater are sensitive to variations in local
84 depositional environment, including local productivity and sedimentation rates, basin
85 connectivity and bottom-water redox state (Bura-Nakić et al., 2018; Andersen et al.,
86 2018; Brüske et al., 2020; Lau et al., 2020), which adds complexity to precise
87 reconstruction of seawater $\delta^{238}\text{U}$ values. However, given that exposure to reducing
88 conditions will result in higher $\delta^{238}\text{U}$ values in the sediments relative to seawater,
89 reducing sediments can provide a robust maximum estimate for seawater values.
90 Further, integration of $\delta^{238}\text{U}$ analysis of reducing sediments with detailed
91 characterization of the hosting facies can be used to track secular changes in seawater
92 $\delta^{238}\text{U}$ values. In this light, shale- and mudstone-hosted U isotope records can be used
93 to independently test whether the widespread anoxia reconstructed for the Ediacaran

94 and Cambrian, on the basis of carbonate archives, accurately reflects ancient marine
95 conditions.

96 In this study, we report new high-resolution $\delta^{238}\text{U}$ data from two marine
97 siliciclastic successions (Daotuo drill core and Yanjia section) (Fig. 1) in the Yangtze
98 block, South China, which span the terminal Ediacaran to Cambrian Stage 3 (ca.
99 551–515 Ma). We focus on U-enriched silicified shale, shale and mudstone, given that
100 the presence of authigenic U enrichments in these lithologies can provide an archive
101 of seawater $\delta^{238}\text{U}$ values, independent of that of shallow carbonates. We measured
102 $\delta^{238}\text{U}$ values from these lithologies, and coupled these to trace element and iron
103 speciation analyses, in order to provide new insights into global seawater $\delta^{238}\text{U}$
104 evolution and compare these to carbonate $\delta^{238}\text{U}$ records.

105 **2. Geological background**

106 The Daotuo drill core, collected from Songtao County of northeastern Guizhou
107 Province, South China, is interpreted to record a weakly restricted mid-depth slope
108 environment during the early Cambrian (Wei et al., 2017). The studied Daotuo drill
109 core samples were collected from the upper Liuchapo Formation to the Jiumenchong
110 Formation, which comprise black chert, black shale, mudstone and calcareous
111 mudstone (Fig. 1). The upper Liuchapo Formation spans the Ediacaran-Cambrian
112 boundary (ca. 542 Ma), based on U-Pb zircon geochronology (Chen et al., 2015a).
113 The lower Jiumenchong Formation contains a polymetallic sulfide-rich layer whose
114 age is 521 ± 5 Ma based on Re-Os dating (Xu et al., 2011) or younger than 522.7 ± 4.9
115 Ma based on U-Pb zircon dating (Wang et al., 2012) of correlated strata in other

116 sections from South China. The Yanjia section is exposed in Chun'an County of
117 Zhejiang Province, South China and interpreted to have been deposited in a deep
118 basin, relatively well connected to the open ocean (Wang et al., 2018). The Yanjia
119 section comprises the Piyuancun Formation and the overlying Hetang Formation, both
120 of which are composed of organic-rich chert, siliceous shale and black shale. The
121 Piyuancun and Hetang formations in the Yanjia section can be correlated to the
122 Liuchapo and Jiumenchong formations in the Daotuo drill core section, respectively
123 (cf. Wang et al., 2018).

124 Stratigraphic correlations on the Yangtze block are shown in Fig. 1, including
125 two sections from the inner shelfal and intrashelf basinal settings (Wei et al., 2018).
126 The studied strata of the Daotuo drill core and Yanjia section are highly condensed in
127 the Cambrian Fortunian and Stage 2 (ca. 541–521 Ma), compared with more
128 expanded carbonate successions in the Xiaotan and Yanjiahe sections (cf. Wei et al.,
129 2018; Dahl et al., 2019). Most samples in this study (middle and upper Jiumenchong
130 and Hetang formations) were deposited during Cambrian Age 3 (ca. 520–515 Ma), an
131 interval during which deposition of chert, black shale and siliceous-calcareous
132 mudstones was widespread across the Yangtze block.

133 **3. Materials and methods**

134 The studied samples with relatively low Ca concentrations (< 3%) were carefully
135 selected in order to avoid the effects of any carbonate components and obvious
136 late-stage veins, and then analyzed for U isotopic composition as well as trace
137 element concentration and total organic carbon. HF, HNO₃ and HCl acids were used

138 to fully digest the samples. Trace element concentrations of the studied samples were
139 measured on a Thermo Finnigan Element XR ICP-MS at Yale University and Nanjing
140 University with errors lower than 5%. Uranium isotopes were measured on a Thermo
141 Finnigan Neptune Plus MC-ICP-MS at Yale University following column
142 chromatography using UTEVA resin, using the method described in Wei et al. (2018).
143 Long-term reproducibility was better than 0.07‰ (2SD), based on replications of the
144 NOD-A-1 geostandard ($-0.61‰ \pm 0.05$, $n = 5$) and CRM 112a standard ($0.03‰ \pm 0.07$,
145 $n = 42$).

146 From among the studied samples for U isotope analyses, representative ones
147 were selected for iron speciation analyses in order to further constrain the local redox
148 conditions. Iron speciation analyses were completed at Nanjing University and
149 Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences,
150 following the sequential extraction procedure of Poulton and Canfield (2005) in order
151 to analyze highly reactive Fe in carbonate, oxides and magnetite, and following the
152 Cr-reduction method of Canfield et al. (1986) for extraction of pyrite-associated Fe.
153 Iron concentrations of extracted highly reactive Fe were measured on an atomic
154 absorption spectroscope (AAS) and ICP-OES with errors lower than 5%. The yield of
155 pyrite-Fe was better than 90% based on repeated analyses of the Chinese GBW07267
156 pyrite standard. Details of all analytical methods are shown in the Supplementary
157 Materials.

158 **4. Results and discussion**

159 **4.1 Uranium isotopes in uppermost Ediacaran through lower Cambrian**

160 **fine-grained siliciclastic strata: local depositional or global marine redox**
161 **control?**

162 Results of U isotope, Fe speciation, total organic carbon and trace element
163 concentration analyses are shown in Table S1 and Fig. 2. High bulk U/Th ratios
164 (distinctly higher than those of terrestrial detrital materials, $U/Th_{\text{detrital}} = 0.282 \pm 0.102$,
165 2SD) (Cole et al., 2017) and a lack of any clear covariation between bulk U
166 concentrations ($[U]_{\text{bulk}}$), bulk $\delta^{238}\text{U}$ values ($\delta^{238}\text{U}_{\text{bulk}}$) and Al or Th concentrations (Fig.
167 3) suggest only negligible detrital contribution to our reported U isotope signatures.
168 We therefore interpret measured $\delta^{238}\text{U}$ signatures to record the behavior of
169 predominantly authigenic (seawater-sourced) U deposited in the sediments under
170 potentially anoxic conditions. In order to further disentangle marine authigenic signals
171 from any potential detrital signals in the bulk sample U isotope data, we calculated U
172 concentrations and $\delta^{238}\text{U}$ values of marine authigenic uranium ($[U]_{\text{auth}}$ and $\delta^{238}\text{U}_{\text{auth}}$),
173 by using the equations published in Andersen et al. (2017) with a simple Monte Carlo
174 simulation to evaluate the uncertainties on calculated $\delta^{238}\text{U}_{\text{auth}}$ values (see
175 Supplementary materials for detail). The Daotuo drill core and Yanjia section exhibit
176 consistent trends and a wide range of $\delta^{238}\text{U}_{\text{auth}}$ values from -0.63‰ to +0.39‰ and
177 from -0.42‰ to +0.32‰, respectively (Fig. 2). Although $[U]_{\text{auth}}$ and $\delta^{238}\text{U}_{\text{auth}}$ of the
178 studied samples vary greatly in the Daotuo and Yanjia sections, no covariation
179 between $[U]_{\text{auth}}$ and Fe contents but clear covariation between $[U]_{\text{auth}}$ and TOC (total
180 organic carbon) contents (Fig. 4) likely suggests that U precipitation was dominated
181 by bacterially mediated U reduction, rather than abiotic Fe (II)-mediated U reduction

182 (e.g., Stylo et al., 2015), which highlights the importance of organic substrates on U
183 precipitation in the anoxic sediments (e.g., Tribovillard et al., 2006).

184 Samples from the lowest Jiumenchong and Hetang formations (upper Cambrian
185 Stage 2), show strongly positive $\delta^{238}\text{U}_{\text{auth}}$ values (up to +0.39‰) (Fig. 2), equivalent
186 to or slightly higher than the heaviest reported U isotope compositions of modern
187 euxinic sediments (e.g., as high as that of Black Sea unit II) (Andersen et al., 2014).
188 Although the units with high $\delta^{238}\text{U}_{\text{auth}}$ values in the lowest Jiumenchong and Hetang
189 formations display relatively high $[\text{U}]_{\text{auth}}$ and TOC contents (Figs. 2 and 4), given the
190 lack of significant covariation between $\delta^{238}\text{U}_{\text{auth}}$ and TOC (Fig. 4D), such high $\delta^{238}\text{U}_{\text{auth}}$
191 values (up to +0.39‰) are unlikely to have been driven primarily by high organic
192 carbon burial fluxes because increased organic carbon delivery within the sediments
193 generally results in rapid U reduction and more quantitative precipitation of U in the
194 sediments, reducing the U isotopic fractionation between sediments and seawater
195 (Andersen et al., 2018; Brüske et al., 2020; Lau et al., 2020). Instead, we suggest that
196 this stratigraphic interval records greater water column or water-sediment interface
197 reduction of U (rather than reduction within the sediment pile) under highly productive
198 conditions, which is consistent with the U isotopic behavior expected in very highly
199 productive regions (cf. Rolison et al., 2017; Abshire et al., 2020; Cheng et al., 2020).
200 Uranium reduction in an unrestricted water column or at the water–sediment interface
201 may result in a higher effective U isotopic fractionation between the sediment and
202 coeval seawater (Rolison et al., 2017; Andersen et al., 2017; Brüske et al., 2020;
203 Abshire et al., 2020). Nonetheless, even if the U isotope offset between sediment and

204 seawater $\delta^{238}\text{U}$ was large, comparable to the largest offsets ($\sim 0.8\text{‰}$) observed in
205 modern anoxic depositional systems (Rolison et al., 2017; Brüske et al., 2020), high
206 $\delta^{238}\text{U}_{\text{auth}}$ values (up to $+0.39\text{‰}$) recorded here likely reflect near-modern seawater
207 $\delta^{238}\text{U}$ values. In this view, high seawater $\delta^{238}\text{U}$ values in this interval indicate a
208 relatively limited extent of anoxic seawater during late Cambrian Age 2, which is
209 consistent with previously published Mo isotope records (Chen et al., 2015b).

210 In contrast, the Liuchapo and upper Piyuancun formations and the middle to
211 upper Jiumenchong and Hetang formations are marked by low $\delta^{238}\text{U}_{\text{auth}}$ values ($<$
212 -0.6‰) that are notably lower than that of modern seawater (Fig. 2). In fact, these are
213 the most negative shale U isotopic values (as low as -0.63‰) that have ever been
214 reported (cf. Wang et al., 2018). These values likely reflect nearly complete U
215 reduction (which can occur in an isolated basin or in porewaters beneath suboxic
216 bottom water). With near quantitative capture of a U reservoir, $\delta^{238}\text{U}_{\text{auth}}$ values of
217 sediments can approach that of seawater (Noordmann et al., 2015; Andersen et al.,
218 2016, 2018; Bura-Nakić et al., 2018). However, even if there is no appreciable U
219 isotopic difference between sediments and seawater, the remarkably negative $\delta^{238}\text{U}_{\text{auth}}$
220 values in the Liuchapo and upper Piyuancun formations and middle to upper
221 Jiumenchong and Hetang formations imply remarkably low seawater $\delta^{238}\text{U}$ values (as
222 low as -0.63‰) across the Ediacaran-Cambrian boundary and during Cambrian Age 3,
223 suggesting widespread marine anoxia during these intervals.

224 To further determine local depositional conditions and thus constrain U isotopic
225 differences between open seawater and the local sediments, we conducted iron

226 speciation analyses ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ and $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$) and Mo, U enrichment factors (Mo_{EF}
227 and U_{EF}) (see Supplementary materials for calculations). Using the standard iron
228 speciation framework (Poulton and Canfield, 2011), essentially all the samples
229 included in this study were deposited under anoxic—but not persistently and strongly
230 sulfidic—bottom water (Fig. 5A). We do not observe any systematic relationships
231 between $\delta^{238}\text{U}_{\text{auth}}$ and $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$, $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ (Fig. 6), which suggests that redox
232 conditions of local bottom water may have not been the dominant factor controlling
233 $\delta^{238}\text{U}_{\text{auth}}$ values of the studied samples. Covariation of Mo_{EF} and U_{EF} is used to further
234 evaluate the depositional environment of the samples in this study and to compare
235 these with modern low-oxygen marine sedimentary systems (cf. Algeo and
236 Tribovillard, 2009; Tribovillard et al., 2012). As shown in Fig. 5B, most of the
237 samples in this study fall within the iron speciation field characteristic of deposition
238 under anoxic conditions and show a $\text{Mo}_{\text{EF}}\text{--}\text{U}_{\text{EF}}$ trend analogous to that of modern
239 open-ocean settings (cf. Algeo and Tribovillard, 2009; Tribovillard et al., 2012),
240 which with the standard interpretation would suggest that the Yangtze continental
241 margin was likely well-connected to the open ocean during the early Cambrian. A few
242 samples with relatively low Mo_{EF} and U_{EF} values have significantly low $\delta^{238}\text{U}_{\text{auth}}$
243 values, potentially representing a locally suboxic depositional environment with less
244 U isotopic fractionation between the sediments and seawater. Collectively, these
245 observations—Fe speciation and $\text{Mo}_{\text{EF}}\text{--}\text{U}_{\text{EF}}$ covariation—imply that, during the early
246 Cambrian, local bottom waters in these regions were well connected to the open ocean
247 and experienced relatively prolonged intervals of strong anoxia. Taken together, we

248 suggest that swings in $\delta^{238}\text{U}_{\text{auth}}$ values from the Daotuo drill core and Yanjia section
249 were not solely controlled by local variability in basin restriction, organic carbon
250 delivery or bottom water redox conditions. Highly consistent $\delta^{238}\text{U}_{\text{auth}}$ variations in
251 these two sections, in part, reflect frequent fluctuations in seawater $\delta^{238}\text{U}$ values. Most
252 importantly, the anomalously positive $\delta^{238}\text{U}_{\text{auth}}$ values of upper Cambrian Stage 2 and
253 negative $\delta^{238}\text{U}_{\text{auth}}$ values of Stage 3 strata provide evidence, independent of carbonate
254 $\delta^{238}\text{U}$ records, for substantial oscillations in oceanic redox states throughout the
255 Cambrian explosion.

256 **4.2 Reconstruction of seawater $\delta^{238}\text{U}$ from the late Ediacaran to early Cambrian** 257 **via siliciclastic archives**

258 Based on the above Fe speciation and $\text{Mo}_{\text{EF}}\text{--U}_{\text{EF}}$ analyses, we reconstruct
259 temporal changes in seawater U isotopic compositions ($\delta^{238}\text{U}_{\text{SW}}$, Fig. 7C) from the
260 reducing sedimentary records of this study by using +0.8‰, +0.6‰, +0.15‰,
261 respectively, as the U isotopic offsets for 1) authigenic U reduction within the
262 high-productive water column or water-sediment interface with efficient
263 replenishment of dissolved U (Rolison et al., 2017; Brüske et al., 2020); 2) within
264 sulfidic sediments of an unrestricted basin (Holmden et al., 2015; Andersen et al.,
265 2018) and 3) within suboxic sediments (Weyer et al., 2008; Andersen et al., 2016).
266 Although U isotopic behavior in reducing sediments may be more complex,
267 simplified estimation of U isotopic offsets under different local conditions can provide
268 insights into secular changes in ancient $\delta^{238}\text{U}_{\text{SW}}$ values. Despite the relatively

269 low-resolution nature of upper Ediacaran and Cambrian Fortunian $\delta^{238}\text{U}_{\text{auth}}$ data (e.g.,
270 three points from potentially suboxic samples for Fortunian excursion P1 in Fig. 7C)
271 and the errors inherent to estimating an effective U isotopic fractionation, secular
272 changes in $\delta^{238}\text{U}_{\text{SW}}$ reconstructed from siliciclastic rocks are strikingly consistent with
273 correlative carbonate $\delta^{238}\text{U}$ profiles (Fig. 7A). This supports the interpretation that
274 changes in $\delta^{238}\text{U}_{\text{auth}}$ mainly reflect global oceanic redox changes. Further, compared to
275 previous studies of carbonate-hosted U isotopic signatures (Fig. 7A), the new $\delta^{238}\text{U}_{\text{SW}}$
276 curve documented in siliciclastic strata provides a higher-resolution record of global
277 oceanic redox states through Cambrian Age 3, and suggests that this critical interval
278 of the Cambrian explosion is marked by large swings in marine redox states.

279 **4.3 Implications for co-evolution of marine environments and early metazoans**

280 We provide estimates of late Ediacaran to early Cambrian (ca. 551 Ma–515 Ma)
281 seawater $\delta^{238}\text{U}$ records from fine-grained siliciclastic rocks that closely match
282 previous estimates from carbonates (Fig. 7). This provides compelling evidence that
283 the early Cambrian was indeed marked by frequent variations in seawater $\delta^{238}\text{U}$
284 (negative excursion N1–N3 and positive excursion P1–P3 in Fig. 7). These swings
285 demonstrate that there were largescale fluctuations in the marine redox landscape
286 (with the U mass balance being tied foremost to the areal extent of anoxic conditions).
287 The frequently fluctuating redox states of the early Cambrian ocean are likely linked
288 to effects of dynamic nutrient supply, shallow marine productivity and ocean
289 ventilation in the ocean with relatively lower baseline oxygenation level than the
290 modern ocean (cf. Wang et al., 2018; He et al., 2019; Dahl et al., 2019; Wei et al.,

291 2020). Further studies are needed to better constrain the triggers for the dramatic
292 changes in marine redox states during this period. The synchronicity of this dynamic
293 redox variation with animal evolutionary clades, increased physiological and
294 ecological complexity and expansion into a wider range of benthic habitats and water
295 depths may, moreover, not be coincidental. In fact, this concurrence provides further
296 empirical evidence in favor of recent proposals that habitat fragmentation and
297 ecological restructuring mediated by redox instability may have facilitated higher
298 rates of generation of evolutionary novelties and thus enhanced biological innovation
299 and turnover—thus serving as a spur, rather than an impediment, to diversification
300 among animal lineages over this interval (Reinhard et al., 2016; Wood and Erwin,
301 2018). In this light, rather than being an anomalous episode in Earth’s history, the
302 Ediacaran–Cambrian protracted emergence and subsequent rapid radiations of
303 complex animal life (and Ediacaran–Ordovician emergence of modern-style
304 ecological strategies and ecosystem structure) against a backdrop of pronounced
305 environmental instability (Droser et al., 2017; Tarhan et a., 2018; Servais and Harper,
306 2018; Wood et al., 2019), broadly resembles patterns of emergence and turnover
307 characteristic of Sepkoskian Phanerozoic Evolutionary Faunas (e.g., Tarhan et al.,
308 2018).

309 **5. Conclusions**

310 New high-resolution uranium isotope data from two upper Ediacaran through
311 Cambrian Stage 3 siliciclastic sections in South China are reported in this study. Both
312 of the studied sections show mutually consistent, large swings in authigenic $\delta^{238}\text{U}$

313 values. Given that local depositional conditions did not dominate authigenic $\delta^{238}\text{U}$
314 values of the studied samples, we interpret much of this variability to be driven by
315 secular changes in seawater $\delta^{238}\text{U}$ values. Notably high authigenic $\delta^{238}\text{U}$ values in
316 upper Cambrian Stage 2 and lowest Stage 3 suggest that host sediments were
317 deposited in an ocean with limited anoxic seafloor area, whereas anomalously
318 negative authigenic $\delta^{238}\text{U}$ values in the terminal Ediacaran and Cambrian Stage 3 are
319 indicative of extensive deep-marine anoxia. Paired $\delta^{238}\text{U}$ records from marine
320 carbonates (Wei et al., 2018; Zhang et al., 2018; Tostevin et al., 2019; Dahl et al.,
321 2019) and siliciclastic strata strengthens the case that anomalously high $\delta^{238}\text{U}$
322 variability (e.g., Wei et al., 2018; Dahl et al., 2019) is tied to episodic swings in global
323 marine redox states from the late Ediacaran through the early Cambrian (ca. 551
324 Ma–510 Ma), rather than diagenetic overprinting. This bolsters the hypothesis that the
325 diversification of early animals during the Cambrian explosion occurred against a
326 backdrop of (and may even have been mediated by) highly spatiotemporally variable
327 marine redox conditions.

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338 **References**

339 Abshire, M.L., Romaniello, S.J., Kuzminov, A.M., Cofrancesco, J., Severmann, S.,
340 Riedinger, N., 2020. Uranium isotopes as a proxy for primary depositional redox
341 conditions in organic-rich marine systems. *Earth and Planetary Science Letters*
342 529, 115878.

343 Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic
344 systems based on molybdenum–uranium covariation. *Chemical Geology* 268,
345 211-225.

346 Andersen, M.B., Romaniello, S., Vance, D., Little, S.H., Herdman, R., Lyons, T.W.,
347 2014. A modern framework for the interpretation of $^{238}\text{U}/^{235}\text{U}$ in studies of
348 ancient ocean redox. *Earth and Planetary Science Letters* 400, 184-194.

349 Andersen, M.B., Stirling, C. H., Weyer, S., 2017. Uranium Isotope Fractionation.
350 *Reviews in Mineralogy and Geochemistry* 82, 799-850.

351 Andersen, M.B., Vance, D., Morford, J.L., Bura-Nakić, E., Breitenbach, S.F.M., Och,
352 L., 2016. Closing in on the marine $^{238}\text{U}/^{235}\text{U}$ budget. *Chemical Geology* 420,
353 11-22.

354 Andersen, M.B., Matthews, A., Vance, D., Bar-Matthews, M., Archer, C., de Souza,
355 G.F., 2018. A 10-fold decline in the deep Eastern Mediterranean thermohaline
356 overturning circulation during the last interglacial period. *Earth and Planetary*

357 Science Letters 503, 58-67.

358 Basu, A., Sanford, R. A., Johnson, T. M., Lundstrom, C. C., Loffler, F. E., 2014.

359 Uranium isotopic fractionation factors during U(VI) reduction by bacterial

360 isolates. *Geochemica et Cosmochimica Acta* 136, 100-113.

361 Brüske, A., Weyer, S., Zhao, M.Y., Planavsky, N.J., Wegwerth, A., Neubert, N.,

362 Dellwig, O., Lau, K.V., Lyons, T.W., 2020. Correlated molybdenum and uranium

363 isotope signatures in modern anoxic sediments: Implications for their use as

364 paleo-redox proxy. *Geochimica et Cosmochimica Acta* 270, 449-474.

365 Bura-Nakić, E., Andersen, M.B., Archer, C., de Souza, G.F., Marguš, M., Vance, D.,

366 2018. Coupled Mo-U abundances and isotopes in a small marine euxinic basin:

367 Constraints on processes in euxinic basins. *Geochimica et Cosmochimica Acta*

368 222, 212-229.

369 Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The

370 use of chromium reduction in the analysis of reduced inorganic sulfur in

371 sediments and shales. *Chemical Geology* 54, 149-155.

372 Chen, D., Zhou, X., Fu, Y., Wang, J., Yan, D., 2015a. New U-Pb zircon ages of the

373 Ediacaran-Cambrian boundary strata in South China. *Terra Nova* 27, 62-68.

374 Chen, X., Ling, H.F., Vance, D., Shields-Zhou, G.A., Zhu, M., Poulton, S.W., Och,

375 L.M., Jiang, S.Y., Li, D., Cremonese, L., Archer, C., 2015b. Rise to modern

376 levels of ocean oxygenation coincided with the Cambrian radiation of animals.

377 *Nat Commun* 6, 7142.

378 Chen, X., Romaniello, S.J., Herrmann, A.D., Hardisty, D., Gill, B.C., Anbar, A.D.,

379 2018. Diagenetic effects on uranium isotope fractionation in carbonate sediments
380 from the Bahamas. *Geochimica et Cosmochimica Acta* 237, 294-311.

381 Cheng, M., Li, C., Jin, C., Wang, H., Algeo, T.J., Lyons, T.W., Zhang, F., Anbar, A.,
382 2020. Evidence for high organic carbon export to the early Cambrian seafloor.
383 *Geochimica et Cosmochimica Acta*. In press.

384 Cole, D.B., Zhang, S., Planavsky, N.J., 2017. A new estimate of detrital
385 redox-sensitive metal concentrations and variability in fluxes to marine
386 sediments. *Geochimica Et Cosmochimica Acta* 215, 337-353.

387 Dahl, T.W., Connelly, J.N., Li, D., Kouchinsky, A., Gill, B.C., Porter, S., Maloof, A.C.,
388 Bizzarro, M., 2019. Atmosphere-ocean oxygen and productivity dynamics during
389 early animal radiations. *Proc. Natl. Acad. Sci. USA* 116, 19352-19361.

390 Droser, M.L., Tarhan, L.G., Gehling, J.G., 2017. The Rise of Animals in a Changing
391 Environment: Global Ecological Innovation in the Late Ediacaran. *Annual*
392 *Review of Earth and Planetary Sciences* 45, 593-617.

393 He, T., Zhu, M., Mills, B.J.W., Wynn, P.M., Zhuravlev, A.Y., Tostevin, R., Pogge von
394 Strandmann, P.A.E., Yang, A., Poulton, S.W., Shields, G.A., 2019. Possible links
395 between extreme oxygen perturbations and the Cambrian radiation of animals.
396 *Nature Geoscience* 12, 468-474.

397 Holmden, C., Amini, M., Francois, R., 2015. Uranium isotope fractionation in
398 Saanich Inlet: A modern analog study of a paleoredox tracer. *Geochimica et*
399 *Cosmochimica Acta* 153, 202-215.

400 Hood, A.v.S., Planavsky, N.J., Wallace, M.W., Wang, X., Bellefroid, E.J., Gueguen, B.,

401 Cole, D.B., 2016. Integrated geochemical-petrographic insights from
402 component-selective $\delta^{238}\text{U}$ of Cryogenian marine carbonates. *Geology* 44,
403 935-938.

404 Hood, A.v.S., Planavsky, N.J., Wallace, M.W., Wang, X., 2018. The effects of
405 diagenesis on geochemical paleoredox proxies in sedimentary carbonates.
406 *Geochimica et Cosmochimica Acta* 232, 265-287.

407 Lau, K.V., Lyons, T.W., Maher, K., 2020. Uranium reduction and isotopic
408 fractionation in reducing sediments: Insights from reactive transport modeling.
409 *Geochimica et Cosmochimica Acta*. In press.

410 Lyons, T.W., Reinhard, C.T., Planavsky, N.J., 2014. The rise of oxygen in Earth's
411 early ocean and atmosphere. *Nature* 506, 307-315.

412 Noordmann, J., Weyer, S., Montoya-Pino, C., Dellwig, O., Neubert, N., Eckert, S.,
413 Paetzel, M., Böttcher, M.E., 2015. Uranium and molybdenum isotope
414 systematics in modern euxinic basins: Case studies from the central Baltic Sea
415 and the Kyllaren fjord (Norway). *Chemical Geology* 396, 182-195.

416 Och, L.M., Shields-Zhou, G.A., 2012. The Neoproterozoic oxygenation event:
417 Environmental perturbations and biogeochemical cycling. *Earth-Science*
418 *Reviews* 110, 26-57.

419 Poulton, S., Canfield, D., 2005. Development of a sequential extraction procedure for
420 iron: implications for iron partitioning in continentally derived particulates.
421 *Chemical Geology* 214, 209-221.

422 Poulton, S.W., Canfield, D.E., 2011. Ferruginous Conditions: A Dominant Feature of

423 the Ocean through Earth's History. *Elements* 7, 107-112.

424 Reinhard, C.T., Planavsky, N.J., Olson, S.L., Lyons, T.W., Erwin, D.H., 2016. Earth's
425 oxygen cycle and the evolution of animal life. *Proc. Natl. Acad. Sci. USA* 113,
426 8933-8938.

427 Rolison, J.M., Stirling, C.H., Middag, R., Rijkenberg, M.J.A., 2017. Uranium stable
428 isotope fractionation in the Black Sea: Modern calibration of the $^{238}\text{U}/^{235}\text{U}$
429 paleo-redox proxy. *Geochimica et Cosmochimica Acta* 203, 69-88.

430 Servais, T., Harper, D.A.T., 2018. The Great Ordovician Biodiversification Event
431 (GOBE): definition, concept and duration. *Lethaia* 51, 151-164.

432 Sperling, E.A., Frieder, C.A., Raman, A.V., Girguis, P.R., Levin, L.A., Knoll, A.H.,
433 2013. Oxygen, ecology, and the Cambrian radiation of animals. *Proc. Natl. Acad.*
434 *Sci. USA* 110, 13446-13451.

435 Sperling, E.A., Knoll, A.H., Girguis, P.R., 2015. The Ecological Physiology of Earth's
436 Second Oxygen Revolution. *Annual Review of Ecology, Evolution, and*
437 *Systematics* 46, 215-235.

438 Stirling, C.H., Andersen, M.B., Warthmann, R., Halliday, A.N., 2015. Isotope
439 fractionation of ^{238}U and ^{235}U during biologically-mediated uranium reduction.
440 *Geochimica et Cosmochimica Acta* 163, 200-218.

441 Stylo, M., Neubert, N., Wang, Y., Monga, N., Romaniello, S.J., Weyer, S.,
442 Bernier-Latmani, R., 2015. Uranium isotopes fingerprint biotic reduction. *Proc.*
443 *Natl. Acad. Sci. USA* 112, 5619-5624.

444 Tarhan, L.G., Droser, M.L., Cole, D.B., Gehling, J.G., 2018. Ecological Expansion

445 and Extinction in the Late Ediacaran: Weighing the Evidence for Environmental
446 and Biotic Drivers. *Integr. Comp. Biol.* 58, 688-702.

447 Tissot, F.L.H., Chen, C., Go, B.M., Naziemiec, M., Healy, G., Bekker, A., Swart, P.K.,
448 Dauphas, N., 2018. Controls of eustasy and diagenesis on the $^{238}\text{U}/^{235}\text{U}$ of
449 carbonates and evolution of the seawater ($^{234}\text{U}/^{238}\text{U}$) during the last 1.4 Myr.
450 *Geochimica et Cosmochimica Acta* 242, 233-265.

451 Tostevin, R., Clarkson, M.O., Gangl, S., Shields, G.A., Wood, R.A., Bowyer, F.,
452 Penny, A.M., Stirling, C.H., 2019. Uranium isotope evidence for an expansion of
453 anoxia in terminal Ediacaran oceans. *Earth and Planetary Science Letters* 506,
454 104-112.

455 Tribovillard, N., Algeo, T.J., Baudin, F., Riboulleau, A., 2012. Analysis of marine
456 environmental conditions based on molybdenum–uranium
457 covariation—Applications to Mesozoic paleoceanography. *Chemical Geology*
458 324-325, 46-58.

459 Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as
460 paleoredox and paleoproductivity proxies: An update. *Chemical Geology* 232,
461 12-32.

462 Wang, D., Ling, H.-F., Struck, U., Zhu, X.-K., Zhu, M., He, T., Yang, B., Gamper, A.,
463 Shields, G. A., 2018a. Coupling of ocean redox and animal evolution during the
464 Ediacaran-Cambrian transition. *Nature Communications* 9, 2575.

465 Wang, X.L., Planavsky, N.J., Hofmann, A., Saupe, E.E., De Corte, B.P., Philippot, P.,
466 LaLonde, S.V., Jemison, N.E., Zou, H.J., Ossa, F.O., Rybacki, K., Alfimova, N.,

467 Larson, M.J., Tsikos, H., Fralick, P.W., Johnson, T.M., Knudsen, A.C., Reinhard,
468 C.T., Konhauser, K.O., 2018b. A Mesoarchean shift in uranium isotope
469 systematics. *Geochimica Et Cosmochimica Acta* 238, 438-452.

470 Wang, X., Shi, X., Jiang, G., Zhang, W., 2012. New U–Pb age from the basal
471 Niutitang Formation in South China: Implications for diachronous development
472 and condensation of stratigraphic units across the Yangtze platform at the
473 Ediacaran–Cambrian transition. *Journal of Asian Earth Sciences* 48, 1-8.

474 Wei, G.-Y., Ling, H.-F., Li, D., Wei, W., Wang, D., Chen, X., Zhu, X.-K., Zhang, F.-F.,
475 Yan, B., 2017. Marine redox evolution in the early Cambrian Yangtze shelf
476 margin area: evidence from trace elements, nitrogen and sulphur isotopes.
477 *Geological Magazine* 154, 1344-1359.

478 Wei, G.-Y., Planavsky, N.J., Tarhan, L.G., Chen, X., Wei, W., Li, D., Ling, H.-F., 2018.
479 Marine redox fluctuation as a potential trigger for the Cambrian explosion.
480 *Geology* 46, 587-590.

481 Wei, G.-Y., Wei, W., Wang, D., Li, T., Yang, X., Shields, G.A., Zhang, F., Li, G., Chen,
482 T., Yang, T., Ling, H.-F., 2020. Enhanced chemical weathering triggered an
483 expansion of euxinic seawater in the aftermath of the Sturtian glaciation. *Earth
484 and Planetary Science Letters* 539, 116244.

485 Weyer, S., Anbar, A.D., Gerdes, A., Gordon, G.W., Algeo, T.J., Boyle, E.A., 2008.
486 Natural fractionation of $^{238}\text{U}/^{235}\text{U}$. *Geochimica et Cosmochimica Acta* 72,
487 345-359.

488 Wood, R., Bowyer, F., Penny, A., Poulton, S.W., 2018. Did anoxia terminate

489 Ediacaran benthic communities? Evidence from early diagenesis. *Precambrian*
490 *Research* 313, 134-147.

491 Wood, R., Erwin, D.H., 2018. Innovation not recovery: dynamic redox promotes
492 metazoan radiations. *Biol. Rev. Camb. Philos. Soc.* 93, 863-873.

493 Wood, R., Liu, A.G., Bowyer, F., Wilby, P.R., Dunn, F.S., Kenchington, C.G., Cuthill,
494 J.F.H., Mitchell, E.G., Penny, A., 2019. Integrated records of environmental
495 change and evolution challenge the Cambrian Explosion. *Nat. Ecol. Evol.* 3,
496 528-538.

497 Xu, L., Lehmann, B., Mao, J., Qu, W., Du, A., 2011. Re-Os Age of Polymetallic
498 Ni-Mo-PGE-Au Mineralization in Early Cambrian Black Shales of South
499 China--A Reassessment. *Economic Geology* 106, 511-522.

500 Zhang, F., Xiao, S., Kendall, B., Romaniello, S.J., Cui, H., Meyer, M., Gilleaudeau,
501 G.J., Kaufman, A.J., Anbar, A.D., 2018. Extensive marine anoxia during the
502 terminal Ediacaran Period. *Science Advances* 4, eaan8983.

503 Zhang, F., Xiao, S., Romaniello, S.J., Hardisty, D., Li, C., Melezhik, V., Pokrovsky, B.,
504 Cheng, M., Shi, W., Lenton, T.M., Anbar, A.D., 2019. Global marine redox
505 changes drove the rise and fall of the Ediacara biota. *Geobiology* 17, 594-610.

506 **Figure captions**

507 **Figure 1.** Stratigraphic columns of the Daotuo drill core and Yanjia sections, and their
508 correlations to inner shelf Xiaotan section and Gaojiaxi–Yanjiahe section in South China (cf.
509 Wei et al., 2018). The shaded areas represent the correlative stratigraphic units of these
510 sections for the Ediacaran (blue), Cambrian Fortunian and Stage 2 (green) and Stage 3

511 (yellow). The red line represents a Ni-Mo polymetallic layer with an age of 521 ± 5 Ma
512 (Re-Os dating from Xu et al., 2011) or $< 522.7 \pm 4.9$ Ma (U-Pb zircon dating from Wang et al.,
513 2012).

514 **Figure 2.** Uranium isotope ($\delta^{238}\text{U}_{\text{auth}}$) values, iron speciation, U_{auth} concentrations and total
515 organic carbon (TOC) contents of the upper Ediacaran to lower Cambrian Daotuo drill core
516 and Yanjia section. Uranium isotope values are presented as $\delta^{238}\text{U}_{\text{auth}}$ for authigenic uranium
517 in bulk samples. The $\delta^{238}\text{U}_{\text{auth}}$ calculation are shown in Supplementary materials. The error
518 bar represents an overall uncertainty (2SD) of calculated $\delta^{238}\text{U}_{\text{auth}}$ for each sample, using a
519 Monte Carlo approach. The shaded vertical bars are estimated average $\delta^{238}\text{U}$ ranges of
520 suboxic and euxinic sediments (Andersen et al., 2017).

521 **Figure 3.** Cross-plots of (A) bulk U concentration vs. Al concentration, (B) bulk $\delta^{238}\text{U}$ vs. Al
522 concentration, (C) bulk U concentration vs. Th concentration, (D) bulk $\delta^{238}\text{U}$ vs. Th
523 concentration for samples from the Daotuo drill core and Yanjia section. R^2 represents the
524 coefficient of determination of the covariation.

525 **Figure 4.** Cross-plots of (A) authigenic U concentration vs. Fe concentration, (B) authigenic
526 $\delta^{238}\text{U}$ vs. Fe concentration, (C) authigenic U concentration vs. TOC concentration, (D)
527 authigenic $\delta^{238}\text{U}$ vs. TOC concentration for samples from the Daotuo drill core and Yanjia
528 section. R^2 represents the coefficient of determination of the covariation.

529 **Figure 5.** (A) $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ vs. $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ for the samples from the Daotuo drill core and Yanjia
530 section analyzed in this study. The divisions between oxic and anoxic conditions ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} =$
531 $0.22\text{--}0.38$) and between ferruginous and euxinic conditions ($\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}} = 0.7\text{--}0.8$) are derived
532 from Poulton and Canfield (2011). (B) Cross-plots of Mo_{EF} vs. U_{EF} for the samples from the

533 Daotuo drill core and Yanjia section in this study as a proxy for local marine sedimentary
534 environment. The shaded zones for different sedimentary environment of the modern ocean
535 are modified after Algeo and Tribovillard (2009) and Tribovillard et al. (2012). Particulate
536 shuttle zone: the transport of Mo within the water column by Fe-Mn-oxyhydroxide
537 particulates (e.g., as in the Cariaco Basin); Open marine zone: benthic redox variations in
538 modern open-ocean systems; Strongly restricted basin: sedimentary basin weakly connected
539 to the open-ocean (e.g. as in the Black Sea).

540 **Figure 6.** Cross-plots of (A) authigenic $\delta^{238}\text{U}$ vs. $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$, (B) authigenic $\delta^{238}\text{U}$ vs. $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$
541 for the samples in the Daotuo drill core and Yanjia section.

542 **Figure 7.** (A)–(B) Secular changes in U isotopic compositions of carbonates (data from Wei
543 et al., 2018; Zhang et al., 2018; Tostevin et al., 2019; Dahl et al., 2019) and siliciclastic rocks
544 from the late Ediacaran to early Cambrian. (C) Calculated $\delta^{238}\text{U}_{\text{SW}}$ values derived from
545 $\delta^{238}\text{U}_{\text{auth}}$ records in this study. The solid curves are LOWESS smoothing fits for U isotope
546 data. Based on TOC, $\text{Mo}_{\text{EF}}-\text{U}_{\text{EF}}$ and Fe speciation analyses, U isotopic differences between
547 reducing sediment and seawater are estimated to be +0.8‰ for organic-rich anoxic or sulfidic
548 samples with TOC > 5 wt% and Mo_{EF} and $\text{U}_{\text{EF}} > 20$ (purple circles); +0.6‰ for anoxic
549 samples with TOC < 5wt%, Mo_{EF} and $\text{U}_{\text{EF}} > 10$ (orange circles); and +0.15‰ for potentially
550 suboxic samples with Mo_{EF} and $\text{U}_{\text{EF}} < 10$ (gray circles). The shaded vertical bars are
551 estimated average $\delta^{238}\text{U}$ ranges of modern non-skeletal carbonates, suboxic sediments and
552 euxinic sediments (Andersen et al., 2017). N1–N3 and P1–P3 represent negative and positive
553 U isotopic excursions from the late Ediacaran through the early Cambrian.

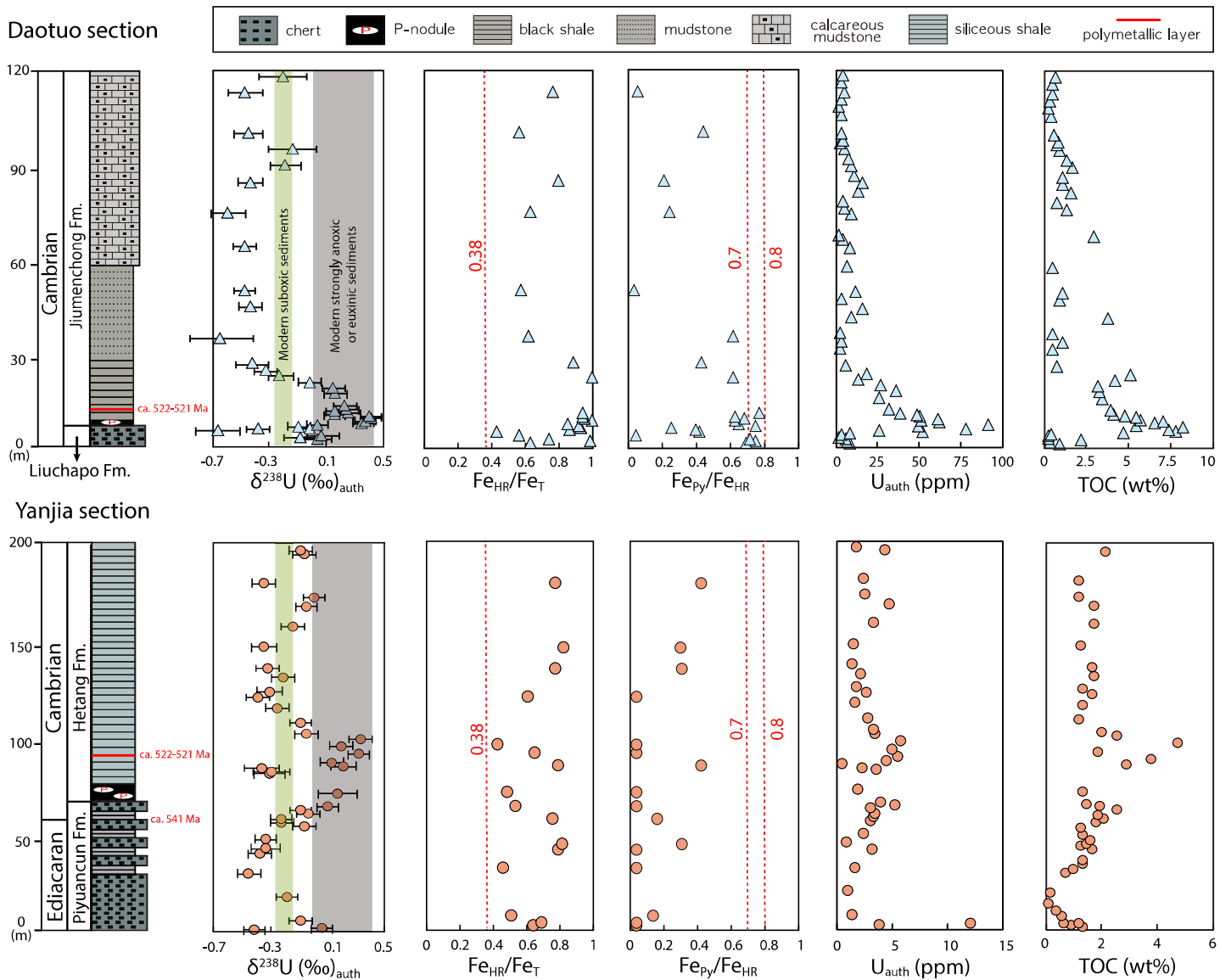
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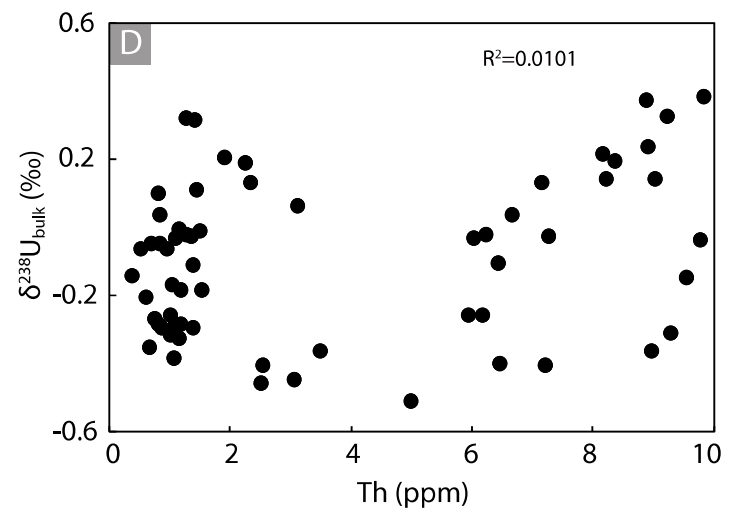
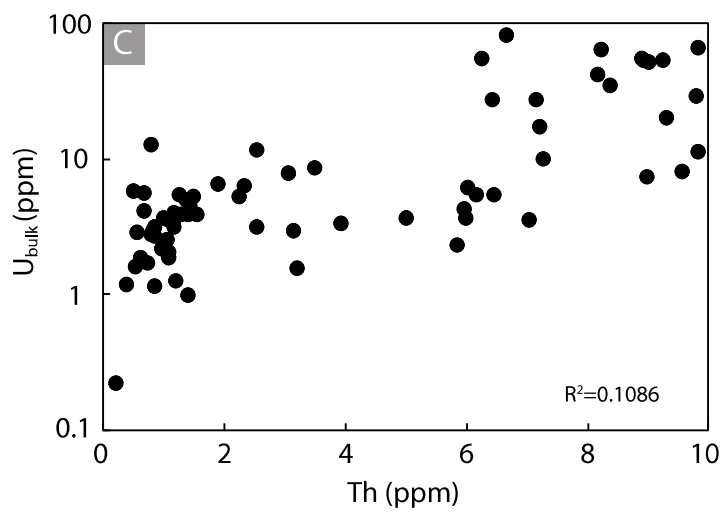
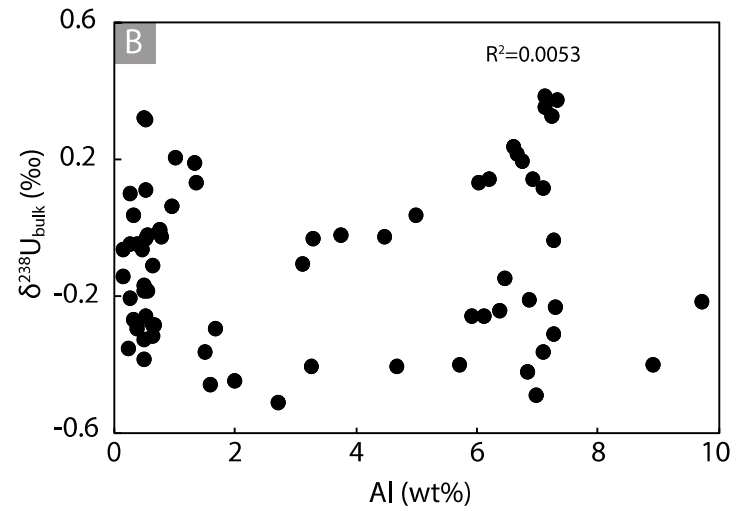
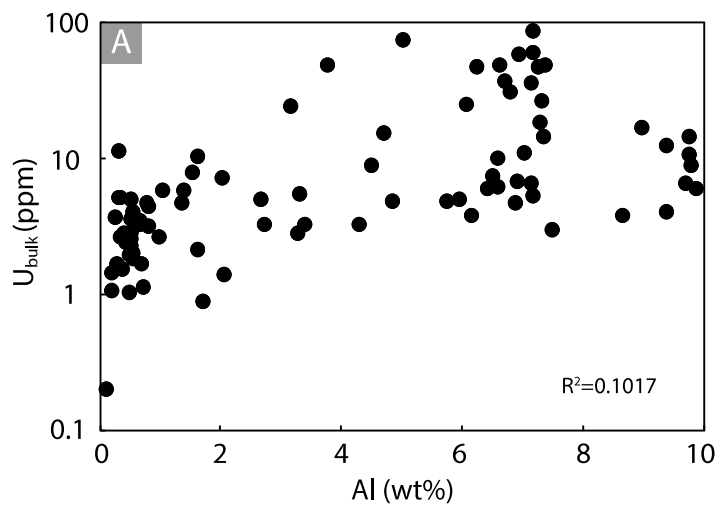


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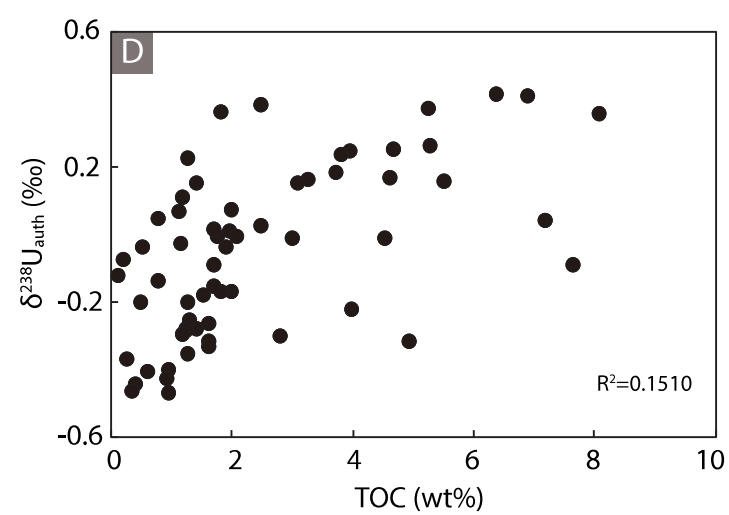
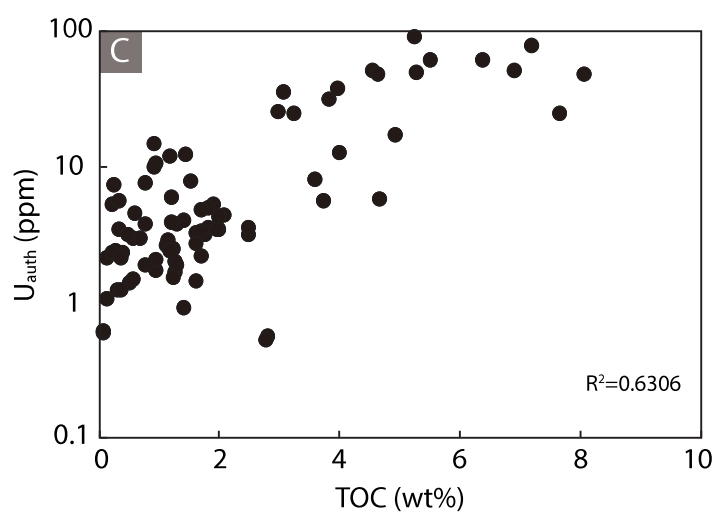
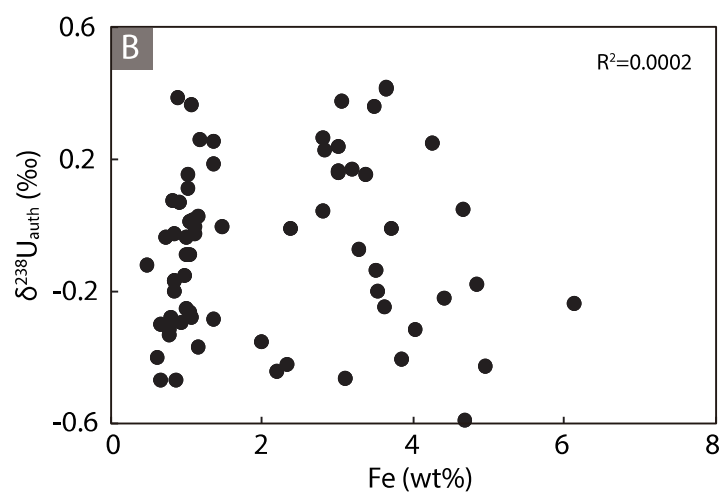
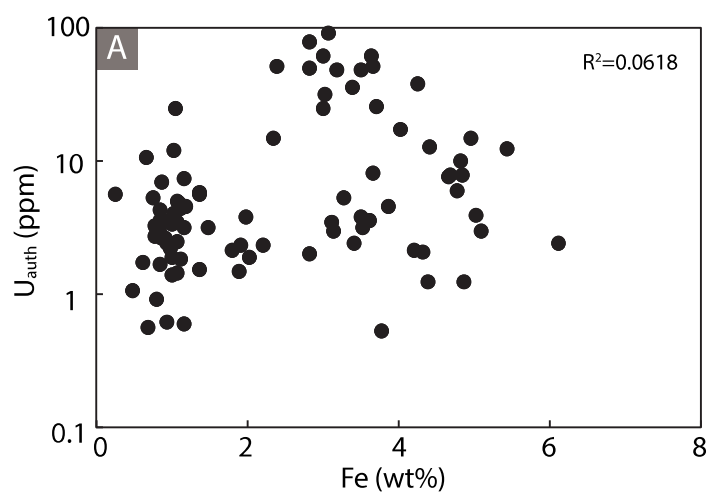


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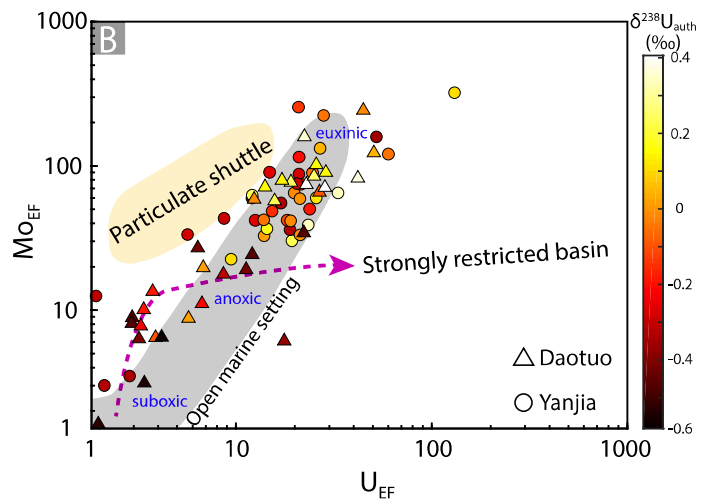
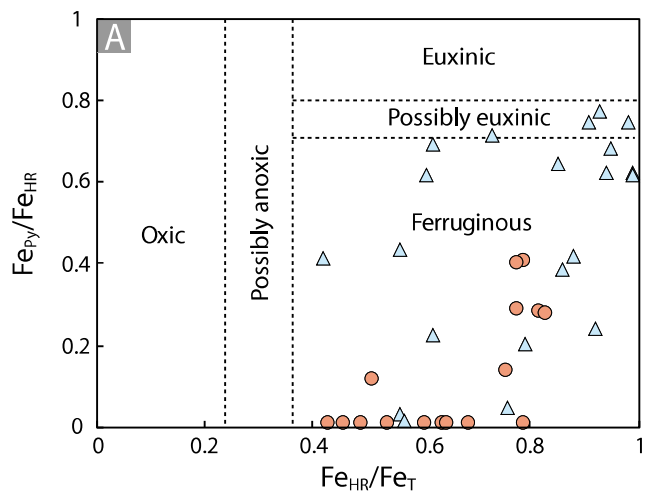


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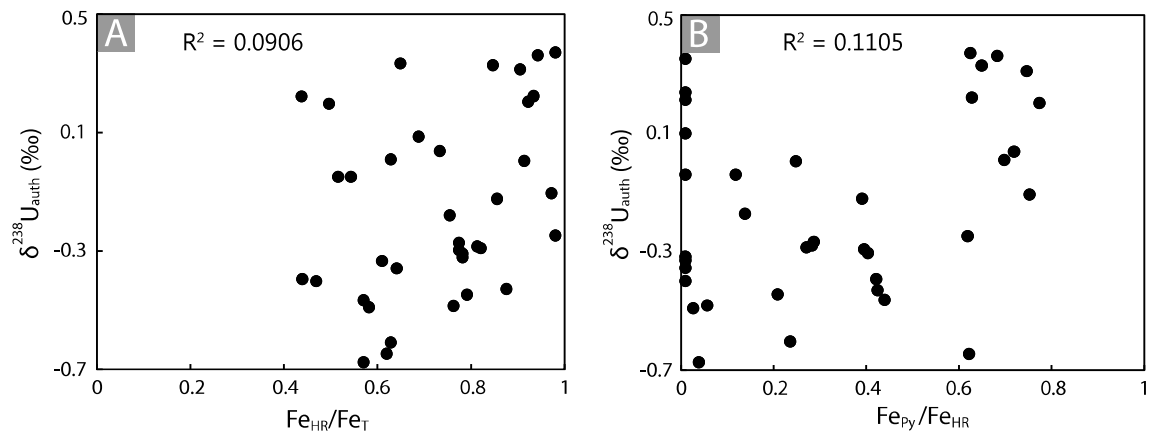
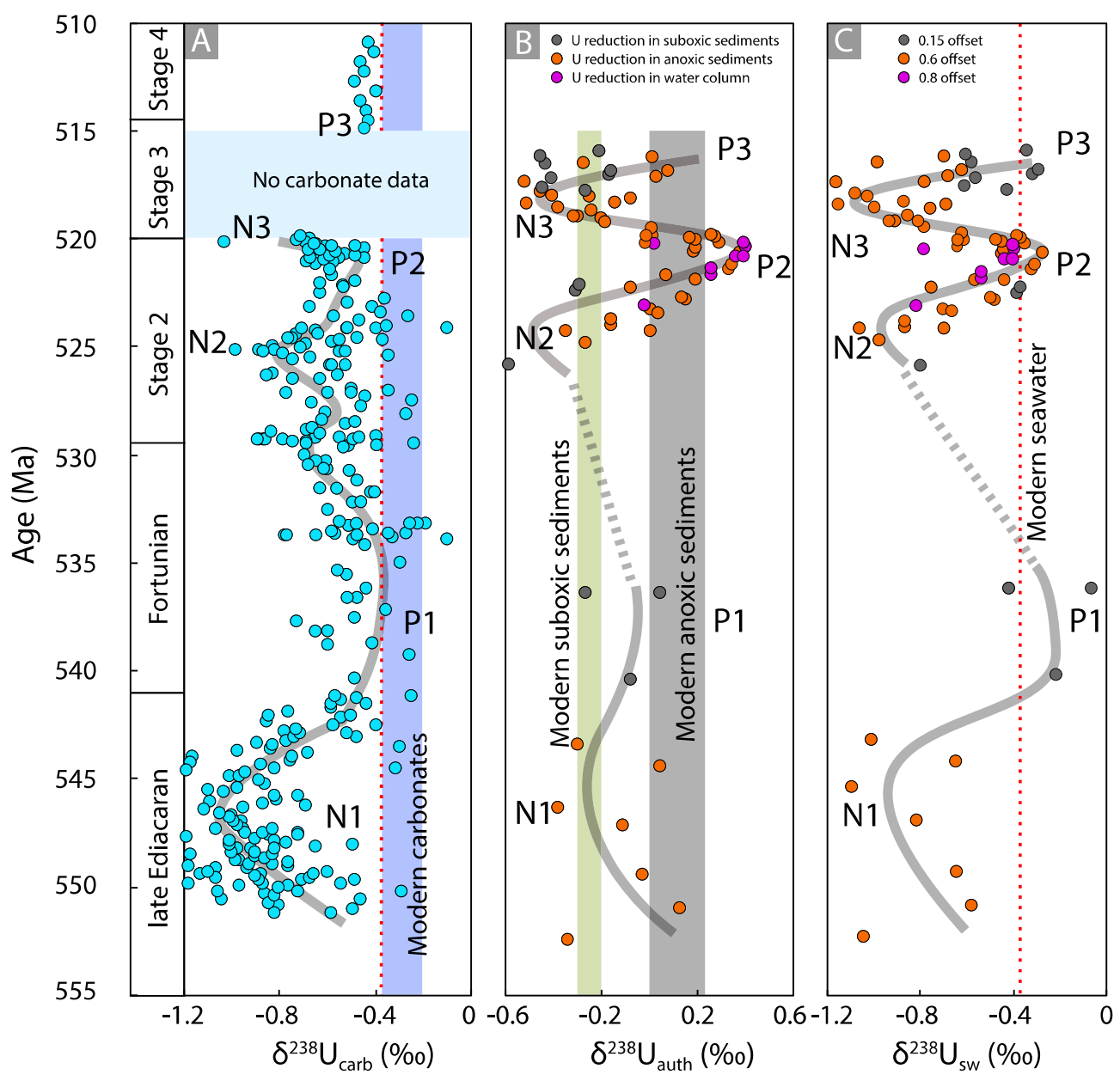


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CRedit author statement

Guang-Yi Wei: Conceptualization, Resources, Methodology, Investigation, Writing-Original draft, Writing-Reviewing and Editing.

Noah Planavsky: Conceptualization, Investigation, Writing-Reviewing and Editing

Lidya Tarhan: Investigation, Writing-Reviewing and Editing

Tianchen He: Resources, Investigation

Graham A. Shields: Writing-Reviewing and Editing

Wei Wei: Resources

Dan Wang: Resources

Hong-Fei Ling: Conceptualization, Writing-Original draft, Writing-Reviewing and Editing

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