

1 **Global oceanic anoxia linked with the Capitanian (Middle Permian) marine mass**
2 **extinction**

3

4 Huyue Song^{1*}, Thomas J. Algeo^{1,2,3}, Haijun Song¹, Jinnan Tong¹, Paul B. Wignall⁴,
5 David P.G. Bond⁵, Wang Zheng⁶, Xinming Chen⁷, Stephen J. Romaniello⁸, Hengye
6 Wei⁹, Ariel D. Anbar¹⁰

7

8 1. State Key Laboratory of Biogeology and Environmental Geology, School of Earth
9 Sciences, China University of Geosciences, Wuhan 430074, China

10 2. Department of Geosciences, University of Cincinnati, Cincinnati, OH 45221, USA

11 3. State Key Laboratory of Geological Processes and Mineral Resources, China
12 University of Geosciences, Wuhan 430074, China

13 4. School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

14 5. Department of Geography, Geology and Environment, University of Hull, Hull, HU6
15 7RX, UK

16 6. Institute of Surface-Earth System Science, School of Earth System Science, Tianjin
17 University, Tianjin, 300072, China

18 7. School of Oceanography, Shanghai Jiao Tong University, Shanghai, 200030, China

19 8. Department of Earth and Planetary Sciences, University of Tennessee Knoxville,
20 Knoxville, TN 37996, USA

21 9. School of Earth Science and Technology, Southwest Petroleum University, Chengdu,
22 610500, China

23 10. School of Earth and Space Exploration, Arizona State University, Tempe, AZ
24 85287, USA

25 * Corresponding author. Email: hysong@cug.edu.cn (HYS)

26

27 **ABSTRACT**

28 The timing and causation of the Capitanian (late Middle Permian) biocrisis remain
29 controversial. Here, a detailed uranium-isotopic ($\delta^{238}\text{U}$) profile was generated for the
30 mid-Capitanian to lower Wuchiapingian of the Penglaitan section (the
31 Guadalupian/Lopingian Permian global stratotype) in South China for the purpose of
32 investigating relationships between the biocrisis and coeval oceanic anoxic events
33 (OAEs). Negative $\delta^{238}\text{U}$ excursions indicate two distinct OAEs, a mid-Capitanian
34 (OAE-C1) and an end-Capitanian (OAE-C2) event. Mass balance modeling shows that
35 the anoxic sink of uranium (F_{anox} ; i.e., the fraction of the total U burial flux) and anoxic
36 seafloor area (F_{area} ; i.e., the fraction of total seafloor area) increased during each OAE.
37 A dynamic mass balance model yields increases of F_{anox} from <30 % to >60 % and F_{area}
38 from ~1% to ~4-7% during each OAE. These two OAEs coincided with two extinction
39 episodes during the Capitanian biocrisis, supporting a causal relationship between
40 oceanic anoxia and mass extinction during the Middle Permian. The most likely driver

41 of middle to late Capitanian global warming and oceanic anoxia was episodic
42 magmatism of the Emeishan Large Igneous Province.

43

44 **Keywords:** Guadalupian–Lopingian boundary; biocrisis; uranium isotopes; Emeishan
45 LIP; global warming; Penglaitan

46

47 **1. Introduction**

48 The Capitanian mass extinction, characterized by genus-level extinction rates of
49 42-61% (Stanley and Yang, 1994; Clapham et al., 2009; Stanley, 2016), was
50 particularly severe for shallow-marine taxa including fusulinacean foraminifers, corals,
51 bivalves, and ammonoids (Shen and Shi, 2009; Wignall et al., 2009; Bond et al., 2010).
52 This event also affected terrestrial ecosystems and resulted in a mass extinction of land
53 vertebrates (Retallack et al., 2006). The timing and number of episodes of the
54 Capitanian biocrisis remain controversial, with proposals for either a mid-Capitanian
55 (Wignall et al., 2009; Bond et al., 2010) or an end-Capitanian event (Shen and Shi,
56 2009; Shen et al., 2020). Although a plethora of mechanisms have been proposed for
57 this extinction, including marine anoxia, volcanism, sea-level fall, ocean acidification,
58 and climatic change (Zhou et al., 2002; Isozaki et al., 2007; Wignall et al., 2009; Bond
59 et al., 2010, 2015, 2020; Zhang et al., 2015; Wei et al., 2016), no consensus regarding
60 its causation has been reached to date.

61 Uranium isotopes in marine carbonates ($\delta^{238}\text{U}_{\text{carb}}$) permit quantitative
62 reconstruction of secular variation in average global-ocean redox conditions. The basis
63 for this proxy is the long residence time of U in seawater (~400 kyr) relative to the
64 oceanic mixing time (~1-2 kyr for the modern) (Ku et al., 1977). Microbially mediated
65 reduction of U(VI) to U(IV) under anoxic conditions at the seafloor results in a
66 substantial decrease in U solubility in seawater (Weyer et al., 2008; Andersen et al.,
67 2014). Because ^{238}U is preferentially reduced and immobilized relative to ^{235}U , the
68 $\delta^{238}\text{U}$ of seawater decreases as its burial flux increases. Thus, a global increase in the
69 extent of ocean anoxic seafloor is expected to cause simultaneous decreases in seawater
70 U concentration [U] and $\delta^{238}\text{U}$. Primary marine carbonates record the $\delta^{238}\text{U}$ of
71 contemporaneous seawater with little fractionation, although precipitation of secondary
72 carbonate cement in the sulfate reduction zone can lead to isotopic shifts of +0.2 ‰ to
73 +0.4 ‰ in bulk-rock $\delta^{238}\text{U}$ (Chen et al., 2018; Tissot et al., 2018). Carbonate $\delta^{238}\text{U}$
74 records have been used to quantitatively reconstruct the extent of seafloor anoxia during
75 several oceanic anoxic events (Lau et al., 2016; Song et al., 2017; Bartlett et al., 2018;
76 Zhang et al., 2018).

77 Although several studies have used elemental or mineralogical proxies to examine
78 local environmental redox variation in Middle Permian sections, with possible
79 implications for ocean anoxic events during the mid-Capitanian (Bond et al., 2015,
80 2020) and end-Capitanian (Zhang et al., 2015; Wei et al., 2016), global-ocean redox
81 proxies such as carbonate $\delta^{238}\text{U}$ have not yet been generated for this event interval.

82 Here, we use the carbonate $\delta^{238}\text{U}$ proxy to document two discrete episodes of global-
83 ocean anoxia during the Capitanian and demonstrate their synchronicity with the two
84 phases of the Middle Permian mass extinction identified in earlier studies.

85

86 **2. Geological background**

87 The Penglaitan section (23°41'43"N, 109°19'16"E; Fig. 1) is the Global Stratotype
88 Section and Point (GSSP) for the Guadalupian-Lopingian series boundary (GLB) as
89 well as of the Capitanian-Wuchiapingian stage boundary (Jin et al., 2006). The GLB is
90 defined by the first appearance datum of the conodont *Clarkina postbitteri postbitteri*
91 at the base of Bed 6k at Penglaitan (Jin et al., 2006). The presence of all biozones from
92 the *Jingondolella shannoni* Zone to the *Clarkina dukouensis* Zone indicates an absence
93 of major hiatuses at Penglaitan (Fig. 2A) (Jost et al., 2014). A total of 53 limestone
94 samples was collected over 22 m of section exposed along the Hongshui River,
95 beginning in the *Jingondolella shannoni* Zone, extending through the upper part of
96 Maokou Formation, and terminating at the base of *Clarkina dukouensis* Zone in the
97 lower Heshan Formation.

98

99 **3. Methods**

100 Weathered surfaces and veins of the samples were trimmed off, and the remaining
101 sample material was cut into small pieces and ground to a fine powder using a ball mill
102 at Wuhan Institute of Geology and Mineral Resources.

103

104 *3.1. Carbon and oxygen isotope analyses*

105 Carbon isotopic compositions were measured using a Thermo Fisher Gasbench II-
106 MAT 253 stable isotope mass spectrometer at the State Key Laboratory of Biogeology
107 and Environmental Geology in the China University of Geosciences (Wuhan). About
108 150-400 μg of powder was placed in a 10 mL Na-glass vial, sealed with a butyl rubber
109 septum, and reacted with 100 % phosphoric acid at 72 °C after flushing with helium
110 using the Gasbench II interface. The $\delta^{13}\text{C}_{\text{carb}}$ composition of the evolved CO_2 gas was
111 measured and reported as per mille variation relative to the Vienna Pee Dee Belemnite
112 (VPDB) standard. Data quality was monitored via repeated analysis of two Chinese
113 national standards, GBW 04416 ($\delta^{13}\text{C} = +1.61 \text{ ‰}$, $\delta^{18}\text{O} = -11.59 \text{ ‰}$) and GBW 04417
114 ($\delta^{13}\text{C} = -6.06 \text{ ‰}$, $\delta^{18}\text{O} = -24.12 \text{ ‰}$), which yielded analytical precisions (2σ) of better
115 than $\pm 0.1 \text{ ‰}$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. In addition, one sample out of every ten was re-analyzed
116 as a replicate to monitor instrumental precision.

117

118 *3.2. Elemental and uranium isotope analyses*

119 Elemental concentrations and uranium isotopes were measured at Arizona State
120 University. About 3-4 g of sample powder were dissolved in 1 M HNO_3 for 24 h and
121 centrifuged to separate insoluble residue from the acid-soluble fraction. The trace
122 element concentrations of carbonates in solution were analyzed using a Thermo iCAP-
123 Q inductively coupled plasma mass spectrometer (ICP-MS). The solution, containing

124 ~500 ng U, was then spiked with an IRMM 3636 uranium double spike to give a
125 $^{233}\text{U}/^{235}\text{U}$ ratio of 2.5 and dried down to homogenize the spike-sample mixture. The
126 sample was redissolved in 3 M HNO_3 , and U was separated from sample matrix using
127 UTEVA Resin (http://www.eichrom.com/products/info/uteva_resin.aspx; see Weyer et
128 al., 2008), with extension of the 3 M HNO_3 matrix elution step to 12 mL in order to
129 completely remove calcium. After column chemistry, the sample was treated twice with
130 a mixture of 2 mL concentrated HNO_3 and 0.2 mL 30 % H_2O_2 to remove residual
131 organics from the resin, and it was then dissolved in 2 % HNO_3 for isotopic analysis.
132 Uranium isotope measurements were performed on a Thermo Scientific Neptune
133 multicollector-inductively coupled plasma mass spectrometer (MC-ICP-MS) and
134 reported as $\delta^{238}\text{U}$ ($^{238}\text{U}/^{235}\text{U}$) relative to the U-isotope standard CRM-145. This
135 standard was analyzed before and after every two samples to correct for minor
136 instrumental drift. The reproducibility of $\delta^{238}\text{U}$ for the standard CRM-145 was better
137 than ± 0.11 ‰ (2 SD, N = 30). The accuracy of U isotope measurements was confirmed
138 by multiple analyses of the secondary standard CRM-129a, which yielded -1.70 ± 0.08 ‰
139 (2 SD, N = 16), conforming to values reported in previous studies (Chen et al., 2018,
140 2021; Zhang et al., 2020). The standard BCR-2 (Columbia River Basalt) yielded values
141 of -0.24 ± 0.12 ‰ (2 SD, N = 14), in agreement with Lau et al. (2016).

142

143 **4. Results**

144 The $\delta^{13}\text{C}_{\text{carb}}$ profile for Penglaitan is similar to that generated in a previous study
145 (Jost et al., 2014). $\delta^{13}\text{C}_{\text{carb}}$ fluctuates between +3.0 ‰ and +5.5 ‰ with moderate
146 positive excursions peaking at ~9.1 m (CPE1; CPE: carbon isotopic positive excursion)
147 and ~20.0 m (CPE2). The GLB is marked by a distinct negative excursion to +3.2 ‰
148 (Fig. 2A; Table S1). Carbonate $\delta^{238}\text{U}$ at Penglaitan ranges from -1.25 ‰ to +0.13 ‰
149 with two distinct negative excursions: UNE-1 (UNE: uranium isotopic negative
150 excursion), from -0.20 ‰ at 3.1 m to -1.25 ‰ at 8.6 m, and UNE-2 from -0.20 ‰ at
151 19.7 m to -0.65 ‰ at 21.6 m, the latter consisting of two peaks (UNE2a at 20.7 m and
152 UNE2b at 21.6 m (Fig. 2B; Table S1). For each episode (i.e., mid-Capitanian versus
153 end-Capitanian), the intervals of the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{238}\text{U}$ excursions overlap broadly,
154 although their peaks are slightly offset: UNE1 precedes CPE1 by ~0.5 m but UNE2
155 lags CPE2 by ~1.5 m. However, second-order excursions in the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{238}\text{U}$
156 profiles at ~12-13 m and ~16-17 m are well-aligned (Fig. 2A-B), documenting a
157 pervasive coupling of the carbon and uranium cycles within the study section.

158

159 **5. Discussion**

160 *5.1. Evidence for primary seawater $\delta^{238}\text{U}$ values*

161 Previous studies have demonstrated that carbonate U isotopes can be altered by
162 various processes (e.g., marine diagenesis, meteoric diagenesis, and dolomitization),
163 yielding mixed primary and secondary signatures in pelagic carbonates (Romaniello et

164 al., 2013; Andersen et al., 2014; Chen et al., 2018; see other references review in Zhang
165 et al., 2020). Here, we investigated relationships between $\delta^{238}\text{U}$ and the U concentration,
166 CaCO_3 content, and Mg/Ca, Mn/Sr, U/Sr and U/Al ratios of the study samples to
167 evaluate the robustness of our U-isotope dataset as a primary record of seawater U
168 isotopes.

169 Post-depositional solution-precipitation reactions in the host carbonate sediment
170 can leach U from calcite, altering Th/U ratios (Chung and Swart, 1990). However, U
171 leaching generally affects U concentrations without altering $\delta^{238}\text{U}$ values (Weyer et al.,
172 2008) due to a lack of fractionation among U isotopes during weathering. Detrital U
173 can mask carbonate U-isotope signals (Stirling et al., 2007; Asael et al., 2013), but there
174 is no significant relationship between U concentration and $\delta^{238}\text{U}$ (Fig. 3A). The study
175 samples also do not show a significant relationship between CaCO_3 content and $\delta^{238}\text{U}$
176 (Fig. 3B). Dolomitization can alter $\delta^{238}\text{U}$ (Romaniello et al., 2013), but most samples
177 in this study (50 of 53 total) exhibit Mg/Ca ratios <0.1 , indicating that dolomitization
178 was insignificant, and there is no significant correlation of Mg/Ca ratios with $\delta^{238}\text{U}$ (Fig.
179 3C).

180 Th is delivered to marine sediments in detrital siliciclastics (mainly clays), and it
181 is relatively immobile in the diagenetic environment. Uranium can accumulate in
182 marine sediments in several forms, including detrital, carbonate-bound, phosphate-
183 bound, and organic-bound fractions (Cumberland et al., 2016). Given typical
184 concentrations in upper continental crust-derived sediments (McLennan et al., 2001)

185 (10.7 ppm Th, 2.8 ppm U), Th/U ratios should be ~4 in sediments without authigenic
186 U enrichment. Wignall and Twitchett (1996) cited Th/U ratios of 2 to 7 for oxic facies
187 versus Th/U ratios of <2 for anoxic facies in which measurable authigenic U enrichment
188 has occurred. The degree of authigenic U enrichment depends on seawater U
189 concentrations, however, and if widespread seafloor anoxia results in seawater U
190 drawdown, then the authigenic U fraction of the sediment will also decline (cf. Algeo,
191 2004). Following initial deposition, U can adsorb/desorb from some phases (especially
192 organics) due to redox changes in sediment porewaters (Cumberland et al., 2016). U in
193 carbonate and phosphate is structurally bound and less subject to secondary
194 remobilization. Diagenetic alteration of U-isotope signals is potentially a concern in
195 carbonate sediments (Hood et al., 2018), but Mn/Sr, U/Sr and U/Al ratios show no
196 correlation with $\delta^{238}\text{U}$ (Fig. 3D-F). In addition, no significant correlation of $\delta^{238}\text{U}$ and
197 U concentrations exists with Al/Ca and Th/Ca (see *S1. Supplemental assessment of*
198 *diagenetic effects* in Supplementary material). These observations provide no evidence
199 of diagenetic alteration of the U-isotopic compositions of the study samples and are
200 thus consistent with well-preserved primary marine geochemical signatures in the
201 Penglaitan section. Leaching of detrital U due to use of 1 N HNO_3 is possible, but
202 testing of different carbonate dissolution protocols (i.e., using acetic acid, HCl and
203 HNO_3) did not yield any significant differences in $\delta^{238}\text{U}_{\text{carb}}$ (see *S2. Tests of multiple*
204 *dissolution protocols* in Supplementary material).

205 Chen et al. (2021) inferred that the uranium isotope compositions of calcite can be
206 affected by anoxic seawater conditions. However, aragonite is relatively less
207 susceptible to this influence, and Permian seas favored aragonite precipitation, as
208 shown by fluid inclusions in marine halite (Lowenstein et al., 2005), although the
209 original carbonate mineralogy of the present study samples is uncertain. In addition,
210 there is no correlation between our $\delta^{238}\text{U}$ profile and local redox variation, as
211 determined from framboidal pyrite (Wei et al., 2016). In summary, there are no
212 relationships of $\delta^{238}\text{U}$ to other geochemical proxies that would imply alteration of U-
213 system chemistry by siliciclastic inputs, dolomitization, or other diagenetic processes.
214 Hence, the $\delta^{238}\text{U}$ profile of this study is regarded as a robust record of variations in
215 contemporaneous seawater U-isotopic composition.

216

217 *5.2. Steady-state and dynamic modeling of the U cycles*

218 Seawater U concentration ([U]) and isotopic compositions are controlled by several
219 factors including the [U] and $\delta^{238}\text{U}$ of rivers and the sink flux of U to anoxic facies. Lau
220 et al. (2016) demonstrated that the principal mechanism for producing large, rapid, and
221 sustained decreases in [U] and $\delta^{238}\text{U}$ (such as those observed in the present study
222 section) is an enhanced flux of U to anoxic facies (i.e., higher F_{anox}). In this study, we
223 employed both dynamic and steady-state U cycle models to quantitatively estimate
224 F_{anox} and concurrent changes in seawater [U] and F_{area} (see *S3. Marine uranium cycle*
225 *modeling* in Supplementary material). The dynamic model results show that F_{anox}

226 increased from <30% to ~70% during UNE-1, decreased to 0-30% between UNE-1 and
227 UNE-2, and then increased again to ~70% during UNE-2 (Fig. 4B; Table S2; note: F_{anox}
228 is 10 in the modern ocean, Montoya-Pino et al., 2010). Seawater [U] decreased from
229 11 nM to 5 nM during UNE-1 and from 13 nM to 8 nM during UNE-2 (Fig. 4A). Mass
230 balance calculations yield F_{area} estimates of ~7% during UNE-1 and ~4% during UNE-
231 2 (Fig. 4D; Table S2; this value is 0.2% in the modern ocean and ~1% in the Middle
232 Permian prior to OAE-C1). The steady-state model yields similar trends for F_{anox} and
233 F_{area} but relatively higher values than the dynamic model (Fig. 4); sensitivity tests
234 demonstrate the general robustness of the modeling output (see *S4. Sensitivity testing*
235 *of model simulations* in Supplementary material).

236

237 *5.3. Two phases of oceanic anoxia during Capitanian*

238 The Penglaitan U-isotope profile and U cycle model reveal two phases of
239 widespread global-ocean anoxia during the middle and late Capitanian (Fig. 2),
240 consistent with the findings of earlier studies making use of local redox proxies (Bond
241 et al., 2015, 2020; Zhang et al., 2015; Wei et al., 2016; Zhang et al., 2021). Pyrite
242 framboid size distributions, sulfur isotopes, and redox-sensitive elements in South
243 China, Spitsbergen, and Arctic Canada provided evidence of a mid-Capitanian anoxic
244 event, although its precise age in the Boreal region is uncertain due to poor age control
245 (Bond et al., 2015, 2020; Zhang et al., 2015; Wei et al., 2016; Zhang et al., 2021). Latest
246 Capitanian anoxia has been inferred on the basis of pyrite framboids and multiple sulfur

247 isotopes in South China and the western USA (Zhang et al., 2015; Wei et al., 2016;
248 Bond et al., 2020). Our U-isotope record, combined with these local redox proxy data,
249 serves to document the existence of two discrete Capitanian OAEs, a finding not
250 previously demonstrated.

251 The specific mechanism triggering oceanic anoxia during the Capitanian remains
252 under investigation. Recent studies have constrained the timing of onset and
253 termination of Emeishan Large Igneous Province (ELIP) magmatism and demonstrated
254 the existence of several eruption phases (reviewed by Shellnutt et al., 2020). ELIP
255 eruptions began during the *J. altudaensis* Zone (~263 Ma) and increased in volume
256 during the *J. xuanhanensis* Zone (~262 Ma) (Sun et al., 2010). New U-Pb ages from
257 zircons in claystones support extensive submarine eruptions during the middle
258 Capitanian (~262.5 Ma) (Yan et al., 2020), with termination of the main phase of ELIP
259 activity was at $\sim 260.0 \pm 0.9$ Ma (Zhong et al., 2014). Coeval ELIP effects have been
260 inferred from spikes in Hg/TOC profiles of the Middle Permian in Spitsbergen, South
261 China, Arctic Canada (Grasby et al., 2016; Huang et al., 2019; Bond et al., 2020) and a
262 positive Hg isotope excursion at Penglaitan (Huang et al., 2019). Recently, Liu et al
263 (2021) used surface-wave tomography to document the existence of a huge magma
264 reservoir and hidden hotspot track related to the ELIP, noting that such hotspot
265 volcanism can liberate potentially catastrophic volumes of greenhouse gases (Fig. 2).

266 Our results demonstrate that the Penglaitan section records two discrete OAEs
267 dating to the middle (*J. altudaensis* to lower *J. xuanhanensis* zones) and the late

268 Capitanian (upper *J. granti* to lower *C. dukouensis* zones). Each OAE may have
269 coincided with a discrete ELIP eruption phase that triggered global climatic warming
270 of ~3-5 °C (Chen et al., 2011; Wang et al., 2020; Zhang et al., 2021) (Fig. 2D), and
271 associated development of marine anoxia through: (1) reduced overturning circulation
272 and increased water-column stratification (Zhang et al., 2021); (2) enhanced subaerial
273 weathering and riverine nutrient fluxes, stimulating high marine primary productivity
274 that consumed dissolved oxygen; and (3) decreased oxygen solubility in seawater. A
275 lessening of oceanic anoxia between UNE1 and UNE2 implies a relative lull in ELIP
276 activity between the two main eruption stages, during which lower and more stable
277 seawater temperatures existed (Chen et al., 2011; Wang et al., 2020) (Fig. 2D).

278 Patterns of $\delta^{13}\text{C}_{\text{carb}}$ variation during the Capitanian and their underlying
279 significance remain in debate (Bond et al., 2010; Jost et al., 2014). In this study, CPE1
280 (~1.5 ‰) spans the upper *J. altudaensis* to basal *J. xuanhanensis* zones, and CPE2
281 (~1.0 ‰) spans the upper *J. granti* to the top of *C. postbitteri hongshuiensis* zones.
282 Whereas CPE2 is well-documented in South China and Japanese sections (Isozaki et
283 al., 2007; Jost et al., 2014; Chen et al., 2011; Wang et al., 2004), CPE1 is less well-
284 established, possibly being represented by a small positive excursion in the *J.*
285 *prexuanhanensis* Zone at Rencunping (Hunan Province, China) (Cao et al., 2018) and
286 *J. prexuanhanensis* to lower *J. xuanhanensis* zones at Penglaitan (Jost et al., 2014). The
287 correlative intervals at Xiongjiachang and Gouchang (Guizhou Province) yielded a

288 large negative excursion (Wignall et al., 2009), but this feature has been attributed to
289 local diagenesis (Jost et al., 2014).

290 Systematic negative covariation between the C- and U-isotope profiles records
291 linkage between organic carbon burial fluxes and global-ocean redox conditions, and
292 the relative timing of $\delta^{13}\text{C}$ versus $\delta^{238}\text{U}$ shifts may indicate patterns of forcings (Fig.
293 2A-B). The UNE1 excursion leads CPE1 with respect to both its start (at ~ 3.6 m vs
294 ~ 5.8 m) and its peak (at 8.6 m vs 9.1 m), which is consistent with expanded oceanic
295 anoxia triggering increased organic burial. The stratigraphic interval between the two
296 main isotopic events is marked by small negative $\delta^{238}\text{U}$ excursions at ~ 13 m and ~ 17
297 m (“minor UNEs”; Fig. 2) that correspond to the termini of rising segments of the $\delta^{13}\text{C}$
298 profile. The observation that the $\delta^{13}\text{C}$ profile is trending positive throughout this
299 interval while negative $\delta^{238}\text{U}$ excursions are short, discrete events suggests that rising
300 marine productivity and organic burial were now driving anoxia, and not the other way
301 around as during the OAE-C1 event. The onset of UNE2 at 18.6 m leads that of CPE2
302 at 19.6 m, suggesting that, once again, oceanic redox changes drove organic carbon
303 burial. This pattern (i.e., redox changes leading organic burial) is consistent with an LIP
304 driver, as massive ocean-surface warming due to emissions of greenhouse gases would
305 cause water-column stratification and stagnation, producing deepwater anoxia that
306 enhanced organic carbon burial (Zhang et al., 2021; cf. Song et al., 2013). Thus, the
307 interplay of our C- and U-isotope records supports two main eruption stages of the ELIP,

308 the first in the mid-Guadalupian (*J. prexuanhanensis* to early *J. xuanhanensis* zones)
309 and the second at the GLB (Fig. 2).

310 The OAE-C2 event was terminated by a rapid decline in $\delta^{13}\text{C}$, whose onset at 20.2
311 m preceded the start of the positive shift in $\delta^{238}\text{U}$ at 21.6 m. This relationship may
312 indicate that, despite continued water-column stagnation related to LIP greenhouse gas
313 release (Zhang et al., 2021; cf. Song et al., 2013), organic C burial fluxes began to falter,
314 probably because of a general deterioration of marine ecosystems and reduced primary
315 production around the GLB. Although other interpretations of the $\delta^{13}\text{C}$ - $\delta^{238}\text{U}$
316 relationships may be possible, the scenario above is consistent with available data
317 regarding ELIP activity and marine biotic patterns during the GLB transition.

318

319 *5.4. The link between oceanic anoxia and biotic crisis*

320 The cause of the biotic crisis during the Capitanian has not been resolved in part
321 because the number and timing of extinctions and their relationships to coeval marine
322 environmental changes are not well established. Our U-isotope records document two
323 OAEs, each coincident with a discrete episode of the biocrisis (Shen and Shi, 2009;
324 Wignall et al., 2009; Bond et al., 2010; Shen et al., 2020) (Fig. 5). During the first
325 episode (i.e., mid-Capitanian OAE-C1), various calcareous algae, fusulinids, and
326 marine invertebrates disappeared in South China (Wignall et al., 2009; Yang et al., 2004)
327 (Fig. 5), Spitsbergen and Arctic Canada (Bond et al., 2015, 2020). At Penglaitan, this
328 event was followed by an interval in which reefs flourished (Huang et al., 2019). During

329 the second episode (i.e., end-Capitanian OAE-C2), reef organisms (including corals,
330 fusulinids, and alataconchids) disappeared together with many ammonoid taxa (Wang
331 and Sugiyama, 2001; Yang et al., 2004; Jin et al., 2006) (Fig. 5). The lesser severity of
332 the Capitanian biocrisis relative to the ‘Big Five’ Phanerozoic mass extinctions
333 (Clapham et al., 2009; Shen et al., 2020) is consistent with its relatively small areas of
334 seafloor anoxia (~4-7%) compared to the end-Permian (>20%) (Zhang et al., 2018) and
335 Late Ordovician mass extinctions (~15%) (Bartlett et al., 2018). In summary, the
336 Capitanian crisis occurred in two episodes, separated by an interlude of improved
337 environmental conditions. Each episode was linked to an oceanic anoxic event that may
338 have been triggered by a phase of intense ELIP magmatism.

339

340 **6. Conclusions**

341 We present a new high-resolution carbonate U-isotope record from the middle
342 Capitanian to earliest Lopingian from the Penglaitan section of South China. The $\delta^{238}\text{U}$
343 profile and marine uranium cycle modeling based thereon reveal two separate global
344 oceanic anoxic events (OAEs), the first during the middle Capitanian *J. altudaensis* to
345 lower *J. xuanhanensis* zones, and the second during the latest Capitanian upper *J. granti*
346 to lower *C. dukouensis* zones. Each OAE coincided with one phase of the Capitanian
347 marine biotic crisis, suggesting a direct causal relationship between anoxia and mass
348 extinction during the Middle Permian. Our results are consistent with eruptions of the

349 Emeishan Large Igneous Province as the trigger for contemporaneous oceanic and
350 climatic changes.

351

352 **Acknowledgments**

353 We thank Professor Shen Shuzhong for discussion of an early version of this
354 manuscript. We thank Du Yong for technical assistance with the carbon and oxygen
355 isotope analyses. This work was supported by the National Natural Science Foundation
356 of China (grants 42172032, 41872033, 41402302 to H-Y.S.) and the Natural
357 Environment Research Council (NE/J01799X/1 to D.P.G.B.).

358

359 **Author contributions:** H-Y.S., A.D.A. designed this research; H-Y.S., H-J.S., H.W.
360 collected the samples; H-Y.S., W.Z., T.J.A., and X.C. performed the elemental and
361 isotopes analysis. R.J.S., T.J.A., W.Z. and H-Y.S. performed the uranium modeling. H-
362 Y.S., H-J.S., P.B.W., D.P.G.B. and J.T. evaluated mass extinction scenarios. H-Y.S.
363 prepared the manuscript with contributions from all co-authors.

364

365 **References**

366 Algeo, T.J., 2004. Can marine anoxic events draw down the trace element inventory
367 of seawater? *Geology* 32, 1057-1060.

368 Andersen, M.B., Romaniello, S., Vance, D., Little, S.H., Herdman, R., Lyons, T.W.,
369 2014. A modern framework for the interpretation of $^{238}\text{U}/^{235}\text{U}$ in studies of
370 ancient ocean redox. *Earth Planet Sci Lett* 400, 184-194.

371 Asael, D., Tissot, F.L.H., Reinhard, C.T., Rouxel, O., Dauphas, N., Lyons, T.W.,
372 Ponzevera, E., Liorzou, C., Chéron, S., 2013. Coupled molybdenum, iron and
373 uranium stable isotopes as oceanic paleoredox proxies during the
374 Paleoproterozoic Shunga Event. *Chem Geol* 362, 193-210.

375 Bartlett, R., Elrick, M., Wheelley, J. R., Polyak, V., Desrochers, A., Asmerom Y.,
376 2018. Abrupt global-ocean anoxia during the Late Ordovician–early Silurian
377 detected using uranium isotopes of marine carbonates. *Proc Natl Acad Sci USA*
378 115, 5896-5901.

379 Bond, D.P.G., Hilton, J., Wignall, P.B., Ali, J.R., Stevens, L.G., Sun, Y.D., Lai, X.L.,
380 2010. The Middle Permian (Capitanian) mass extinction on land and in the
381 oceans. *Earth-Sci Rev* 102, 100-116.

382 Bond, D.P.G., Wignall, P.B., Joachimski, M.M., Sun, Y.D., Savov, I., Grasby, S.E.,
383 Beauchamp, B., Blomeier, D.P., 2015. An abrupt extinction in the Middle
384 Permian (Capitanian) of the Boreal Realm (Spitsbergen) and its link to anoxia
385 and acidification. *Geol Soc Am Bull* 127, 1411-1421.

386 Bond, D.P.G., Wignall, P.B., Grasby, S.E., 2020. The Capitanian (Guadalupian,
387 Middle Permian) mass extinction in NW Pangea (Borup Fiord, Arctic Canada): A
388 global crisis driven by volcanism and anoxia. *Geol Soc Am Bull* 132, 931-942.

389 Cao, C., Cui, C., Chen, J., Summons, R.E., Shen, S.Z., Zhang, H., 2018. A positive C-
390 isotope excursion induced by sea-level fall in the middle Capitanian of South
391 China. *Palaeogeogr Palaeoclimatol Palaeoecol* 505, 305-316.

392 Chen, B., Joachimski, M.M., Sun, Y.D., Shen, S.Z., Lai, X.L., 2011. Carbon and
393 conodont apatite oxygen isotope records of Guadalupian–Lopingian boundary
394 sections: Climatic or sea-level signal? *Palaeogeogr Palaeoclimatol Palaeoecol*
395 311, 145-153.

396 Chen, X.M., Romaniello, S.J., Herrmann, A.D., Anbar, A.D., 2018. Diagenetic effects
397 on uranium isotope fractionation in carbonate sediments from the Bahamas.
398 *Geochim Cosmochim Acta* 237, 294-311.

399 Chen, X.M., Romaniello, S.J., McCormick, M., Sherry, A., Havig, J.R., Zheng, W.,
400 Anbar, A.D., 2021. Anoxic depositional overprinting of $^{238}\text{U}/^{235}\text{U}$ in calcite:
401 When do carbonates tell black shale tales? *Geology* 49, 1193-1197.

402 Clapham, M.E., Shen, S.Z., Bottjer, D.J., 2009. The double mass extinction revisited:
403 reassessing the severity, selectivity, and causes of the end-Guadalupian biotic
404 crisis (Late Permian). *Paleobiology* 35, 32-50.

405 Cumberland, S.A., Douglas, G., Grice, K., Moreau, J.W., 2016. Uranium mobility in
406 organic matter-rich sediments: A review of geological and geochemical
407 processes. *Earth-Sci Rev* 159, 160-185.

408 Grasby, S.E., Beauchamp, B., Bond, D.P.G., Wignall, P.B., Sanei, H., 2016. Mercury
409 anomalies associated with three extinction events (Capitanian crisis, latest
410 Permian extinction and the Smithian/Spathian extinction) in NW Pangea. *Geol*
411 *Mag* 153, 285-297.

412 Henderson, C.M., Davydov, V.I., Wardlaw, B.R., 2012. The Permian Period. In:
413 Gradstein FM, Ogg JG and Schmitz MA et al. (eds.). *The Geologic Time Scale*
414 2012. Amsterdam: Elsevier, 653-679.

415 Hood, A.v.S., Planavsky, N.J., Wallace, M.W., Wang, X., 2018. The effects of
416 diagenesis on geochemical paleoredox proxies in sedimentary carbonates.
417 *Geochim Cosmochim Acta* 232, 265-287.

418 Huang, Y.G., Chen, Z.Q., Wignall, P.B., Grasby, S.E., Zhao, L., Wang, X., Kaiho, K.,
419 2019. Biotic responses to volatile volcanism and environmental stresses over the
420 Guadalupian-Lopingian (Permian) transition. *Geology* 47, 175-178.

421 Isozaki, Y., Kawahata, H., Ota, A., 2007. A unique carbon isotope record across the
422 Guadalupian-Lopingian (Middle-Upper Permian) boundary in mid-oceanic paleo-
423 atoll carbonates: The high-productivity “Kamura event” and its collapse in
424 Panthalassa. *Global Planet Change* 33, 21-38.

425 Jin, Y.G., Shen, S.Z., Henderson, C.M., Wang, X., Wang, W., Wang, Y., Cao, C.,
426 Shang, Q., 2006. The Global Stratotype Section and Point (GSSP) for the
427 boundary between the Capitanian and Wuchiapingian Stage (Permian). *Episodes*
428 29, 253-262.

429 Jost, A.B., Mundil, R., He, B., Brown, S.T., Altiner, D., Sun, Y.D., DePaolo, D.J.,
430 Payne, J.L., 2014. Constraining the cause of the end-Guadalupian extinction with
431 coupled records of carbon and calcium isotopes. *Earth Planet Sci Lett* 396, 201-
432 212.

433 Ku, T.L., Knauss, K., Mathieu, G.G., 1977. Uranium in the open ocean: concentration
434 and isotopic composition. *Deep-Sea Res* 24, 1005-1017.

435 Lau, K.V., Maher, K., Altiner, D., Kelley, B.M., Kump, L.R., Lehrmann, D.J., Silva-
436 Tamayo, J.C., Weaver, K.L., Yu, M., Payne, J.L., 2016. Marine anoxia and
437 delayed Earth system recovery after the end-Permian extinction. *Proc Natl Acad*
438 *Sci USA* 113, 2360-2365.

439 Liu, Y., Li, L., Wiik, J.V., Li, A., Fu, Y.V., 2021. Surface-wave tomography of the
440 Emeishan large igneous province (China): Magma storage system, hidden hotspot
441 track, and its impact on the Capitanian mass extinction. *Geology* 49, 1032-1037.

442 Lowenstein, T.K., Timofeeff, M.N., Kovalevych, V.M., Horita, J., 2005. The major-
443 ion composition of Permian seawater. *Geochim Cosmochim Acta* 69, 1701-1719.

444 McLennan, S.M., 2001. Relationships between the trace element composition of
445 sedimentary rocks and upper continental crust. *Geochem Geophys Geosys* 2,
446 2000GC000109.

447 Montoya-Pino, C., Weyer, S., Anbar, A.D., Pross, J., Oschmann, W., van de
448 Schootbrugge, B., Arz, H.W., 2010. Global enhancement of ocean anoxia during
449 Oceanic Anoxic Event 2: A quantitative approach using U isotopes. *Geology* 38,
450 315-318.

451 Retallack, G.J., Metzger, C.A., Greaver, T., Jahren, A.H., Smith, R.M., Sheldon,
452 N.D., 2006. Middle–Late Permian mass extinction on land. *Geol Soc Am Bull*
453 118, 1398-1411.

454 Romaniello, S.J., Herrmann, A.D., Anbar, A.D., 2013. Uranium concentrations and
455 $^{238}\text{U}/^{235}\text{U}$ isotope ratios in modern carbonates from the Bahamas: Assessing a
456 novel paleoredox proxy. *Chem Geol* 362, 305-316.

457 Shellnutt, J.G., Pham, T.T., Denyszyn, S.W., Yeh, M.W., Tran, T.A., 2020. Magmatic
458 duration of the Emeishan large igneous province: Insight from northern Vietnam.
459 *Geology* 48, 457-461.

460 Shen, S.Z., Shi, G., 2009. Latest Guadalupian brachiopods from the Guadalupian/
461 Lopingian boundary GSSP section at Penglaitan in Laibin, Guangxi, South China
462 and implications for the timing of the pre-Lopingian crisis. *Palaeoworld* 18, 152-
463 161.

464 Shen, S.Z., Yuan, D.X., Henderson, C.M., Wu, Q., Zhang, Y.C., Zhang, H., Mu, L.,
465 Ramezani, J., Wang, X.D., Lambert, L.L., Erwin, D.H., Hearst, J.M., Xiang, L.,
466 Chen, B., Fan, J.X., Wang, Y., Wang, W.Q., Qi, Y.P., Chen, J., Qie, W.K., Wang,
467 T.T., 2020. Progress, problems and prospects: An overview of the Guadalupian
468 Series of South China and North America. *Earth-Sci Rev* 211, 103412.

469 Song, H.Y., Tong, J., Algeo, T.J., Horacek, M., Qiu, H., Song, H.J., Tian, L., Chen,
470 Z.Q., 2013. Large vertical $\delta^{13}\text{C}_{\text{DIC}}$ gradients in Early Triassic seas of the South
471 China craton: Implications for oceanographic changes related to Siberian Traps
472 volcanism. *Glob Planet Change* 105, 7-20.

473 Song, H.Y., Song, H.J., Algeo, T.J., Tong, J., Romaniello, S.J., Zhu, Y., Chu, D.,
474 Gong, Y., Anbar, A.D., 2017. Uranium and carbon isotopes document global-
475 ocean redox-productivity relationships linked to cooling during the Frasnian-
476 Famennian mass extinction. *Geology* 445, 887-890.

477 Stanley, S.M., 2016. Estimates of the magnitudes of major marine mass extinctions in
478 Earth history. *Proc Natl Acad Sci USA* 113, E6325-E6334.

479 Stanley, S.M., Yang, X., 1994. A double mass extinction at the end of the Paleozoic
480 era. *Science* 266, 1340-1344.

481 Stirling, C.H., Andersen, M.B., Potter, E.K., Halliday, A.N., 2007. Low-temperature
482 isotopic fractionation of uranium. *Earth Planet Sci Lett* 264, 208-225.

483 Sun, Y.D., Lai, X., Wignall, P.B., Widdowson, M., Ali, J.R., Jiang, H., Wang, W.,
484 Yan, C., Bond, D.P.G., Védérine, S., 2010. Dating the onset and nature of the
485 Middle Permian Emeishan large igneous province eruptions in SW China using
486 conodont biostratigraphy and its bearing on mantle plume uplift models. *Lithos*
487 119, 20-33.

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

492 Wang, X., Sugiyama, T., 2001. Middle Permian rugose corals from Laibin, Guangxi,
493 South China. *J Paleontol* 75, 758-782.

494 Wang, W., Cao, C., Wang, Y., 2004. The carbon isotope excursion on GSSP
495 candidate section of Lopingian-Guadalupian boundary. *Earth Planet Sci Lett* 220,
496 57-67.

497 Wang, W.Q., Garbelli, C., Zhang, F.F., Zheng, Q.F., Shen, S.Z., 2020. A high-
498 resolution Middle to Late Permian paleotemperature curve reconstructed using
499 oxygen isotopes of well-preserved brachiopod shells. *Earth Planet Sci Lett* 540,
500 116245.

501 Wei, H., Wei, X., Qiu, Z., Song, H.Y., Shi, G., 2016. Redox conditions across the G–
502 L boundary in South China: Evidence from pyrite morphology and sulfur isotopic
503 compositions. *Chem Geol* 440, 1-14.

504 Weyer, S., Anbar, A.D., Gerdes, A., Gordon, G.W., Algeo, T.J., Boyle, E.A., 2008.
505 Natural fractionation of $^{238}\text{U}/^{235}\text{U}$. *Geochim Cosmochim Acta* 72, 345-359.

506 Wignall P.B., Twitchett R.J., 1996. Oceanic anoxia and the end Permian mass
507 extinction. *Science* 272, 1155-1158.

508 Wignall, P.B., Sun, Y.D., Bond, D.P.G., Izon, G., Newton, R.J., Védrine, S.,
509 Widdowson, M., Ali, J.R., Lai, X., Jiang, H., Cope H., 2009. Volcanism, mass
510 extinction, and carbon isotope fluctuations in the Middle Permian of China.
511 *Science* 324, 1179-1182.

512 Yan, H., Pi, D.H., Jiang, S.Y., Hao, W., Konhauser, K.O., 2020. New constraints on
513 the onset age of the Emeishan LIP volcanism and implications for the
514 Guadalupian mass extinction. *Lithos* 360-361, 105441.

515 Yang, X., Liu, J., Shi, G., 2004. Extinction process and patterns of Middle Permian
516 fusulinaceans in southwest China. *Lethaia* 37, 139-147.

517 Zhang, B.L., Wignall, P.B., Yao, S.P., Hu, W.X., Liu, B., 2021. Collapsed upwelling
518 and intensified euxinia in response to climate warming during the Capitanian
519 (Middle Permian) mass extinction. *Gondwana Res* 89, 31-46.

520 Zhang, F.F., Romaniello, S.J., Algeo, T.J., Lau, K.V., Clapham, M.E., Richoz, S.,
521 Herrmann, A.D., Smith, H., Horacek, M., Anbar, A.D., 2018. Multiple episodes
522 of extensive marine anoxia linked to global warming and continental weathering
523 following the latest Permian mass extinction. *Sci Adv* 2018; 4: e1602921.

524 Zhang, F.F., Lenton, T.M., Rey, A.D., Romaniello, S.J., Chen, X.M., Planavsky, N.J.,
525 Clarkson, M.O., Dahl, T.W., Lau, K.V., Wang, W.Q., Li, Z.H., Zhao, M.Y.,
526 Isson, T., Anbar, A.D., 2020. Uranium isotopes in marine carbonates as a global
527 ocean paleoredox proxy. A critical review. *Geochim Cosmochim Acta* 287, 27-
528 49.

529 Zhang, G., Zhang, X., Li, D., Farquhar, J., Shen, S., Chen, X., Shen, Y., 2015.
530 Widespread shoaling of sulfidic waters linked to the end-Guadalupian (Permian)
531 mass extinction. *Geology* 43, 1091-1094.

532 Zhong, Y.T., He, B., Mundil, R., Xu, Y.G., 2014. CA-TIMS zircon U-Pb dating of
533 felsic ignimbrite from the Binchuan section: Implications for the termination age
534 of Emeishan large igneous province. *Lithos* 204, 14-19.

535 Zhou, M.F., Malpas, J., Song, X.Y., Robinson, P.T., Sun, M., Kennedy, A.K., Lesher,
536 C.M., Keays, R.R., 2002. A temporal link between Emeishan large igneous
537 province (SW China) and the end-Guadalupian mass extinction. *Earth Planet Sci*
538 *Lett* 196, 113–122.

539

540 **Figure captions**

541

542 **Fig. 1. Global paleogeography of Middle Permian (~260 Ma).** Adapted from Ron
543 Blakey, <https://deeptimemaps.com/>, ©2016 Colorado Plateau Geosystems Inc. Red star
544 is the Penglaitan section. Red circles are sites of oceanic anoxia area during the
545 Guadalupian. A: South China (Zhang et al., 2015; Wei et al., 2016); B: Spitsbergen
546 (Bond et al., 2020); C: Sverdrup Basin (Bond et al., 2015); D: Nevada (Zhang et al.,
547 2015).

548

549 **Fig. 2. Chemostratigraphy of the Penglaitan study section:** (A) $\delta^{13}\text{C}_{\text{carb}}$, (B)
550 carbonate $\delta^{238}\text{U}$; (C) percent anoxic seafloor area (F_{area}); (D) Tropical sea surface
551 temperature (SST) curves. Abbreviations: Fm.: Formation; *J.*: *Jingondolella*; *alt.*:
552 *altudaensis*; *pre.*: *prexuanhanensis*; *C.p.h.*: *Clarkina postbitteri hongshuiensis*; *C.p.p.*:
553 *Clarkina postbitteri postbitteri*; *C.d.*: *Clarkina dukouensis*. CPE: carbon isotope
554 positive excursion; UNE: uranium isotope negative excursion, ELIP: Emeishan Large
555 Igneous Province. The geochronologic ages are from Henderson et al. (2012) and Shen
556 et al. (2020). Tropical SST curves are from Chen et al. (2011) and Wang et al. (2020);
557 Hg peak intervals in mid-Capitanian from Grasby et al. (2016) and Bond et al. (2020)
558 and in end-Capitanian from Huang et al. (2019); hotspot volcanism from Liu et al.
559 (2021); ELIP interval from Shellnutt et al. (2020).

560

561 **Fig. 3.** Comparison of $\delta^{238}\text{U}$ ratios to U concentration (A), CaCO_3 (B), Mg/Ca ratios
562 (C), Mn/Sr ratios (D), U/Sr (E), and U/Al (F).

563

564 **Fig. 4. Marine U-cycle mass balance model under steady state and dynamic state:**

565 (A) Seawater U concentrations (nM); (B) Fractional U removal to anoxic sink, F_{anox} ;

566 (C) Seawater $\delta^{238}\text{U}$ data (gray), LOWESS-smoothed curve (black, overlapped by the

567 dynamic model curve), and dynamic model curve (blue); (D) Modeled changes in

568 anoxic seafloor changes, F_{area} .

569

570 **Fig. 5. Relationship between anoxic seafloor (F_{anoxic}) and two stages of mass**

571 **extinction during the Capitanian.** Taxon ranges for mid-Capitanian are from Wignall

572 et al. (2009) and for end-Capitanian from Jin et al. (2006) and Wang and Sugiyama

573 (2001).

574