Article:
Song, H, Algeo, TJ, Song, H et al. (8 more authors) (2023) Global oceanic anoxia linked with the Capitanian (Middle Permian) marine mass extinction. Earth and Planetary Science Letters, 610. 118128. ISSN 0012-821X

https://doi.org/10.1016/j.epsl.2023.118128

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

Huyue Song[1*], Thomas J. Algeo[1,2,3], Haijun Song[1], Jinnan Tong[1], Paul B. Wignall[4], David P.G. Bond[5], Wang Zheng[6], Xinming Chen[7], Stephen J. Romaniello[8], Hengye Wei[9], Ariel D. Anbar[10]

1. State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan 430074, China
2. Department of Geosciences, University of Cincinnati, Cincinnati, OH 45221, USA
3. State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China
4. School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
5. Department of Geography, Geology and Environment, University of Hull, Hull, HU6 7RX, UK
6. Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin, 300072, China
7. School of Oceanography, Shanghai Jiao Tong University, Shanghai, 200030, China
8. Department of Earth and Planetary Sciences, University of Tennessee Knoxville, Knoxville, TN 37996, USA

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

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

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

ABSTRACT

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

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

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

1. Introduction

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

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

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

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

2. Geological background

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

3. Methods

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

3.1. Carbon and oxygen isotope analyses

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

3.2. Elemental and uranium isotope analyses

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

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

4. Results

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

5. Discussion

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

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

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

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

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

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

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

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

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

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

5.3. Two phases of oceanic anoxia during Capitanian

The Penglaitan U-isotope profile and U cycle model reveal two phases of widespread global-ocean anoxia during the middle and late Capitanian (Fig. 2), consistent with the findings of earlier studies making use of local redox proxies (Bond et al., 2015, 2020; Zhang et al., 2015; Wei et al., 2016; Zhang et al., 2021). Pyrite framboid size distributions, sulfur isotopes, and redox-sensitive elements in South China, Spitsbergen, and Arctic Canada provided evidence of a mid-Capitanian anoxic event, although its precise age in the Boreal region is uncertain due to poor age control (Bond et al., 2015, 2020; Zhang et al., 2015; Wei et al., 2016; Zhang et al., 2021). Latest 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 ~260.0 ± 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

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

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

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

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

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

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

5.4. The link between oceanic anoxia and biotic crisis

The cause of the biotic crisis during the Capitanian has not been resolved in part because the number and timing of extinctions and their relationships to coeval marine environmental changes are not well established. Our U-isotope records document two OAEs, each coincident with a discrete episode of the biocrisis (Shen and Shi, 2009; Wignall et al., 2009; Bond et al., 2010; Shen et al., 2020) (Fig. 5). During the first episode (i.e., mid-Capitanian OAE-C1), various calcareous algae, fusulinids, and marine invertebrates disappeared in South China (Wignall et al., 2009; Yang et al., 2004) (Fig. 5), Spitsbergen and Arctic Canada (Bond et al., 2015, 2020). At Penglaitan, this 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 $\delta^{238}U$
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

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

Acknowledgments

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

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

References

Algeo, T.J., 2004. Can marine anoxic events draw down the trace element inventory 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 $^{238}U/^{235}U$ 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., Wheeley, 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 $^{238}U/^{235}U$ 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.

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

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

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

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

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

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

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 $\delta^{13}C_{DIC}$ 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.

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

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

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

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

Wang, W.Q., Garbelli, C., Zhang, F.F., Zheng, Q.F., Shen, S.Z., 2020. A high-resolution Middle to Late Permian paleotemperature curve reconstructed using oxygen isotopes of well-preserved brachiopod shells. Earth Planet Sci Lett 540, 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 $^{238}U/^{235}U$. 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

Figure captions

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

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

561 **Fig. 3.** Comparison of $\delta^{238}U$ 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 $\delta^{238}U$ 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