Rapid expansion of oceanic anoxia immediately before the end-Permain mass extinction

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Periods of oceanic anoxia have had a major influence on the evolutionary history of Earth and are often contemporaneous with mass extinction events. Changes in global (as opposed to local) redox conditions can be potentially evaluated using U system proxies. The intensity and timing of oceanic redox changes associated with the end-Permian extinction horizon (EH) were assessed from variations in $\delta^{238}$U/$\delta^{235}$U and Th/U ratios in a carbonate section at Dawen in southern China. The EH is characterized by shifts toward lower $\delta^{238}$U values (from $-0.37\%$ to $-0.65\%$), indicative of an expansion of oceanic anoxia, and higher Th/U ratios (from 0.06 to 0.42), indicative of drawdown of U concentrations in seawater. Using a mass balance model, we estimate that this isotopic shift represents a sixfold increase in the flux of U to anoxic facies, implying a corresponding increase in the extent of oceanic anoxia. The intensification of oceanic anoxia coincided with, or slightly preceded, the EH and persisted for an interval of at least 40,000 to 50,000 y following the EH. These findings challenge previous hypotheses of an extended period of whole-ocean anoxia prior to the end-Permian extinction.

The end-Permian extinction represents the largest mass extinction in Earth history, with the demise of an estimated 90% of all marine species (1). While it has been extensively studied, the exact nature and cause of the end-Permian extinction remains the subject of intense scientific debate. Proposed kill mechanisms have included a nearby supernova, bolide impacts, periods of extreme volcanism (e.g., Siberian Traps), extensive glaciation, and widespread oceanic anoxia (2). Evidence for shallow-ocean anoxia in conjunction with the end-Permian mass extinction is widespread (3–6), but the intensity and timing of oceanic redox changes remain uncertain (7–10). Recent hypotheses have invoked the release of hydrogen sulfide gas (H$_2$S) from seawater as a kill mechanism (11–13). Such models call upon strong expansion of oceanic anoxia below the oxygenated surface layer to allow buildup of H$_2$S, followed by an upward excursion of the chemocline that releases the poisonous gas into the atmosphere (13). In this study, we examine the $\delta^{238}$U/$\delta^{235}$U and Th/U (thorium/uranium) ratios in a carbonate section spanning the end-Permian extinction horizon (EH) to evaluate the timing and scale of these possibilities. Samples for this study were collected from the Dawen section of the Yangtze Block in southern China (Fig. 1), which has been correlated with the global stratotype section and point (GSSP) of the Permian-Triassic boundary at Meishan (14).

Due to the geochemical properties of U, the ratio of $^{238}$U/$^{235}$U can be used as a tool to investigate the history of ocean oxygenation at a global scale, as opposed to the local redox information provided by most commonly used proxies. The long residence time (~500 ky) of U in the oceans leads to a homogeneous U concentration in seawater (15, 16), as well as to a homogenous U isotopic composition (17–19). The low-temperature redox transition of U (from $U^{4+}$ to $U^{6+}$) is the primary cause of $^{238}$U/$^{235}$U fractionation on Earth, with the reduced species preferentially enriched in $^{238}$U (18–22). During times of oceanic anoxia, the flux of reduced U to anoxic facies (such as black shales) increases, preferentially removing $^{238}$U from seawater. The loss of isotopically heavy U drives seawater to lighter isotopic compositions (23). Changes in the U isotopic ratios of organic-rich sediments have been used to study oceanic redox conditions during the Cretaceous (23). Here, we apply this isotopic system to Late Permian and Early Triassic carbonate rocks. Existing evidence indicates that carbonates record the $^{238}$U/$^{235}$U ratio of the seawater in which they were deposited (18, 19), suggesting that ancient carbonates that retain a primary signal of U isotopes can be used to estimate relative changes in ocean oxygenation.

Results and Discussion

In the Dawen section, the average U isotopic composition of samples deposited prior to the EH ($\delta^{238}$U = $-0.37\%$) is very close to that of modern seawater ($\delta^{238}$U = $-0.41 \pm 0.03\%$ (19)). This observation suggests that the fraction of U removed to reducing sinks during the late Permian was similar to that of the modern ocean. The Dawen section exhibits an abrupt and significant change in $\delta^{238}$U at the EH (Fig. 2) to values averaging $-0.65\%$. The $\delta^{238}$U ratios of pre- and post-EH samples are significantly different ($p < 0.0001$; two-tailed student’s t-test with a significance level of $\alpha = 0.01$). A few isotopically light samples are present below the EH (~118 and ~97 cm), which may provide evidence of brief episodes of transient intensification of oceanic anoxia preceding the end-Permian mass extinction. This inference is supported by evidence from additional geochemical proxies in other studies (7) (see SI Text for further discussion).

The shift toward lighter U isotopic compositions after the extinction event is consistent with an increase in the deposition of isotopically heavy U in anoxic facies. The isotopic composition of U in seawater is ultimately controlled by the relative sizes and isotopic signatures of the major sources and sinks of U to the ocean. A simple box model of the oceanic U budget for the modern and end-Permian oceans is shown in Fig. 3. Invoking mass balance, we calculated the approximate increase in anoxic sedimentation in the end-Permian ocean as:

$$\delta^{238}U_{\text{input}} = \left(1 - f_{\text{anoxic}}\right) \times \delta^{238}U_{\text{other}} + f_{\text{anoxic}} \times \delta^{238}U_{\text{anoxic}}.$$  

[1]

Here, $f_{\text{anoxic}}$ represents the fraction of U deposited in anoxic facies and $\delta^{238}U_{\text{anoxic}}$ represents the $\delta^{238}U$ values of the anoxic and “other” (i.e., nonanoxic) sinks. Following Montoya-Pino, et al. (23), we assume: (1) isotopically constant U input from rivers [the largest source of U to the ocean (24)] over geologic time with
a value of $-0.3\%$; (2) a constant isotope fractionation between seawater and anoxic/euxinic environments of $+0.5\%$; and (3) a constant ($\pm 0.1\%$) isotope fractionation between seawater and the sum of other sinks, including ferromanganese oxide, hydrothermal, and suboxic sediments. Suboxic sediments, which are defined by their low oxygen concentrations in the bottom water (e.g., 0.2–2 mL O$_2$/L H$_2$O (25)), are likely to represent the largest nonanoxic sink (24) and are known to accumulate U with a small fractionation ($\pm 0.1\%$) relative to seawater (19). Based on the assumptions above, $\delta^{238}$U$_{\text{input}} = -0.3\%$, $\delta^{238}$U$_{\text{other}} = -0.55\%$ (i.e., $-0.65 + 0.1\%$), and $\delta^{238}$U$_{\text{anoxic}} = -0.15\%$ (i.e., $-0.65 + 0.5\%$). These values yield an estimated sixfold increase in the flux of U to anoxic facies in conjunction with the EH.

Th/U ratios serve as an additional and independent line of evidence for ocean redox changes in conjunction with the end-Permian extinction. Previous workers have used Th/U ratios in reduced sediments as a proxy for ocean redox chemistry (5). As Th has only one redox state (Th$^{4+}$), its concentration in sediments is unaffected by redox conditions. On the other hand, U is a redox-sensitive metal and is readily removed from seawater as insoluble U$^{4+}$ under reducing conditions (26–28), thus concentrating U relative to Th in anoxic facies. An increase in anoxic sedimentation reduces the concentration of U in seawater as more U is sequestered in organic-rich sediments. Because the U concentration of carbonates is related to the U concentration of the seawater in which they are deposited (29, 30), an increase in anoxic sedimentation results in an increase in the Th/U ratio of carbonate sediments. At Dawen, average Th/U ratios increase from 0.06 below the EH to 0.42 above the EH (Fig. 2). This increase reflects a decrease in the U content of seawater, possibly by a factor of $\sim 7$x if Th concentrations remained constant. A change in seawater U concentrations of this magnitude is consistent with the sixfold expansion of oceanic anoxic inferred from our $\delta^{238}$U data, and is also consistent with the sharp decrease in U concentrations across the Permian-Triassic boundary (PTB) previously reported from a carbonate section in Oman (10). Although a lower U concentration would imply a shorter ocean residence time, even if reduced tenfold the U residence time would have been 50–100 times longer than the time scale for ocean mixing. Therefore, it is reasonable to assume that $\delta^{238}$U and Th/U provide information at global scale.

Although the study section has undergone burial diagenesis, the U and carbonate C isotope profiles are unlikely to have been
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but, rather, of a rapid and sustained change in oceanographic
signal is consistent with proxies recording local redox conditions
within the Panthalassic Ocean (31, 32). In contrast, the steady and
prolonged decline of carbonate δ13C seen in many stratigraphic
sections prior to the EH has been used to argue for an extended
period of ocean stagnation and whole-ocean anoxia (2). If so, δ238U and Th/U in carbonates should track δ13C. This behavior is not observed (Fig. 2). The existence of an unconformable surface in the Dawen section at the level of the EH (Fig. 2) makes exact assessment of the timing of global redox changes unattainable. If the missing section is equivalent to beds 25 and 26 at Meishan, it would represent a hiatus of about 50,000–75,000 y (14). However, we note that the δ13C curve for Dawen (see Fig. 5 in ref. 14) shows an almost unbroken shift toward more negative values across the contact, suggesting that the hiatus was of limited duration. These data indicate that the abruptness of the shifts in δ238U and Th/U ratios at the EH (Fig. 2) was the result not of a missing section but, rather, of a rapid and sustained change in oceanographic conditions. The persistence of low δ238U and high Th/U ratios through the 10 m of section above the EH that were analyzed in this study (Fig. 2) indicates that intensified anoxia persisted a minimum of ~40,000–50,000 y following the end-Permian extinc
tion (14, 33, 34).*

While our data do not support the extended period of whole-
sea anoxia prior to the EH inferred from δ13C records, they do not invalidate the idea that the end-Permian mass extinction was caused by oceanic oxygen depletion and a subsequent build-
up and release of H2S from the oceans, as inferred on the basis of
geochemical, isotopic, and biomarker studies (3–6, 8). Com-
monly, models of this process invoke an extended period of
shluggish ocean circulation, producing deep-ocean anoxia and ac-
cumulation of H2S. This interpretation was previously challenged by
numerical models of the ocean-climate system suggesting that
the deep ocean was most likely well ventilated throughout the
Late Permian-Early Triassic interval (35). We propose that the
geochemical data and numerical models can be reconciled by
hypothesizing expanded and more intense oxygen-minimum
zones at middepths in the late-Permian ocean (7, 9, 32). Suboxic
deep-ocean conditions during the Late Permian prior to the EH
(9, 32) would have decreased the U concentration of the ocean,
lowering the residence time of U in seawater and setting the
stage for the rapid shift in Th/U at the EH observed at Dawen
(Fig. 2). Th/U ratios of pre-EH carbonates at Dawen are signifi-
cantly higher than Th/U ratios in modern marine carbonates,
supporting the hypothesis that U was substantially drawn down
in latest Permian seawater relative to modern seawater. Suboxic
deep-ocean conditions would not have markedly altered the U
isotope budget of the global ocean, as suboxic sedimentation does not fractionate U isotopes with the same magnitude as anoxic
sedimentation (19, 23). Uranium isotopes would have shifted
measurably only with an increase in anoxic sedimentation. How-
ever, transient disturbances to Late Permian oceans [e.g., warm-
ing or an increase in continually derived nutrients (9)] may have resulted in brief episodes of expansion of oxygen-minimum
zones before the end-Permian extinction, as reflected in light
δ238U ratios below the EH (~118 and ~97 cm). Expansion of oxygen-minimum zones could have introduced H2S into the
photic zone (9) if the upper boundary of the former shallowed
sufficiently (to <100 m water depth). This could then result in
release of toxic gasses into shallow-marine environments and
the atmosphere (12), similar to the degassing of H2S in modern
oxygen-minimum zones in Namibia (36).

A model of ocean chemistry with widespread regions of
relatively warm and poorly oxygenated deep water and localized
intermittent sulfide maxima at midwater depths (i.e., within
the oxygen-minimum zone) satisfies not only δ13C evidence pre-
viously used to argue for sustained oceanic anoxia prior to the
EH, but also explains the observed geochemical and biogeochem-
signatures associated with anoxia/euxinia at the close of the
Permian. Development of middepth sulfide maxima poised on
the edge of expansion into the surface water layer could account
for the presence of biomarkers indicative of photic-zone euxinia
in shallow-marine sections prior to the EH (4, 6) without requir-
ing anoxia of the deep ocean, which would alter the U isotope
budget of seawater. Evidence from the U system indicates wide-
spread oceanic anoxia only became pronounced and persistent
at, or just preceding the EH. Thus, this study supports the pos-
sibility of H2S as a killing mechanism, but calls for buildup of H2S in the oxygen-minimum zone rather than prolonged accumula-
in the deep ocean. This interpretation should be tested by
investigating U proxies across other Permian-Triassic sections and
by examining the fidelity with which carbonate sediments
record and preserve primary U proxy signatures.

Methods
Study samples were powdered and dissolved using dilute (∼1 M) hydrochlo-
ic acid, leaving any noncarbonate species present (e.g., organics, pyrite,
siliclastics, etc.) intact and nonparticipatory in subsequent procedures.
The dissolved material was dried and reconstituted in 3 M HNO3. Approxi-
ately 10% of the material was used for trace element analyses, with data
obtained using a Thermo X-series quadrupole ICP-MS at the W. M. Keck
Laboratory for Environmental Biogeochemistry at Arizona State University
(ASU). The remaining 90% of the dissolved carbonate material was passed
through a column containing Eichrom® UTEVA resin, following the pro-
dule procedure outlined in Weyer, et al. (19) to separate uranium from the
matrix. Uranium isotope measurements were performed on a ThermoFinnigan
Neptune MC-ICP-MS instrument at Arizona State University (ASU, W.M. Keck
Laboratory for Environmental Biogeochemistry), utilizing a 236U, 233U dou-
ble-spike MC-ICP-MS procedure described in Weyer, et al. (19). The isotopic
composition of the double spike used is 236U/233U = 1.00494, 238U/233U
= 0.00958, 235U/233U = 0.000108. Samples were spiked to achieve 236U and
235U signals of ~2.5 times the voltage on the least abundant measured
isotope, 238U. This spiking technique maximizes the counting statistics on
the spike masses, while minimizing the tailing contributions at mass 235.
All measured isotopes of U were collected by a Faraday cup collector array,
utilizing 1011 ohm resistors for all masses. Samples dissolved in 2% HNO3
were introduced with an Apex-Q sample introduction system. Optimum
precision was obtained running samples at ~100 ppb U. The U isotope stan-
ards SRM950a and CRM129a were measured bracketing samples as checks
for run reproducibility and consistency. External reproducibility based on
multiple runs of the SRM950a and CRM129a standards over the course of
this study is shown in SI Text. The U isotopic compositions of the samples
are reported as relative to the U isotope standard SRM950a.

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