Temperature-driven nutrient recycling and euxinia as a marine mass extinction mechanism

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Extreme warming at the end-Permian induced profound changes in marine biogeochemical cycling and animal habitability, leading to the largest extinction in Earth’s history. However, a causal mechanism for the extinction that explains the different proxy evidence has yet to be found. By combining recent modeling developments with global and local redox observations, we show that a temperature-driven increase in microbial respiration can reconcile reconstructions of the spatial distribution of euxinia and seafloor anoxia spanning the Permian/Triassic transition. We illustrate how enhanced metabolic rates would have strengthened upper ocean nutrient recycling, and thus shoaled and intensified the oxygen minimum zones eventually causing euxinic waters to expand onto continental shelves, poisoning benthic habitats. Finally, we find that the temperature effect on microbial activity can account
for some of the decline in carbon isotopes at the end-Permian with the implication that car-
bon release as inferred from those changes is likely overestimated. Our findings present
a novel view of the sensitive interconnections between temperature, microbial metabolism,
ocean redox state and carbon cycling during the end-Permian mass extinction with potential
far-ranging implications for the interpretation of carbon cycle perturbations during Earth
history.

Climate warming driven by volcanic greenhouse gas release is widely regarded as the under-
lying driver for the largest metazoan extinction event in Earth’s history at the end of the Permian
Period when ~90% of marine species were eliminated\(^1,2\). Although the extinction event itself has
been intensely studied and is relatively well characterized, the specific physical and/or biogeo-
chemical environmental changes that drove biodiversity loss in the ocean are uncertain\(^3\). Proxy
evidence reveals a 7-10\(^\circ\)C increase in sea surface temperature occurring in as little as \(\sim 39\) kyr\(^4-6\)
(Fig. 1a+d), the development of (photic-zone) euxinia (waters containing sulphide\(^7\)), an expan-
sion in the extent of seafloor anoxia\(^8,9\), and a decrease in the carbon isotopic signature recorded in
carbonates\(^10\) (\(\delta^{13}C_{\text{carb}}\), Fig. 1e), all approximately reaching their nadir at the extinction horizon\(^11\)
(EH, \(\sim 251.94\) Ma).

Proposed explanations linking these observations with the extinction all require reduced oxy-
genation of the ocean, but fundamentally diverge at this point. In particular, previous 3D Earth
system model (ESM) studies have required either a sustained collapse of global ocean circulation
in conjunction with a much weaker biological pump\(^12\), or a well ventilated end-Permian ocean
in conjunction with a much stronger biological pump driven by enhanced nutrient (phosphate) availability\textsuperscript{13,14}. However, other modelling work\textsuperscript{15} has demonstrated that increasing the ocean phosphate inventory sufficiently to create widespread subsurface euxinia, not only requires an excessive increase in phosphate availability, but also results in near-global anoxia in the deep sea\textsuperscript{16} which is in conflict with paleoredox estimates from uranium isotope records\textsuperscript{9,17} (Fig. 1b+c). Other explanations focus on reducing oxygen availability throughout the ocean as a whole, either through the oxidation of methane released from hydrates\textsuperscript{13} or of a massive reservoir of dissolved organic matter\textsuperscript{18}, or via warming driven by the CO\textsubscript{2} release associated with volcanism\textsuperscript{19,20}. These carbon release mechanisms can also drive a pronounced decline in $\delta^{13}$C\textsubscript{carb}. However, a gradient in $\delta^{13}$C\textsubscript{carb} from surface to subsurface records\textsuperscript{21} suggests a vertical partitioning in ocean geochemistry occurred and that there is much more to the event than carbon release and climate warming. Here we reconcile the varying proxy observations and provide new insights into the controls on subsurface euxinia and hence marine extinction mechanisms, by recognising the important role of temperature in stimulating microbial respiration and thus dictating the redox profile in the water column.

Oxygen availability in the water column generally decreases from well-mixed surface waters (few tens of meters), to the oxygen minimum zone (OMZ, typically at a depth of a few hundreds of meters). Along with vertical ocean mixing, this gradient is controlled by the remineralization of particulate organic matter (POM) which consumes oxygen and releases inorganic nutrients (and carbon) that can be returned to the surface to fuel new primary productivity\textsuperscript{22}. Critical here is the interplay between reactivity and sinking rate of POM, as it controls the shape of the remineraliza-
tion rate depth profile (i.e. the scale depth of POM remineralization) and, thus, the intensity and depth of OMZs\textsuperscript{16,23}. We posit that a further factor, and the key to understanding how the marine environment changed across the Permian/Triassic boundary (P/Tr), is ocean temperature\textsuperscript{24}.

**A mechanistic representation of the biological pump**

To demonstrate the importance of a warming ocean in driving subsurface euxinia and potentially widespread extinction across shallow marine environments, we simulate redox distributions for a range of P/Tr conditions using the cGENIE ESM\textsuperscript{25,26}. We modify the widely used ’static’ representation of the biological pump (i.e. an invariant POM remineralization depth profile\textsuperscript{27}), to allow us to explicitly account for the impact of ocean warming at the end-Permian on POM remineralization (SI). In addition, to reflect the shallower remineralization profile inferred prior to the rise of pelagic calcifiers in the early Mesozoic\textsuperscript{23}, we decrease the sinking rate of POM in the model by \(\sim22\%\) – scaled to the smaller mean animal biovolume at the end-Permian (\textsuperscript{28}, SI). Finally, we account for changes in POM remineralization as reactive POM compounds react with sulphide (\(\text{H}_2\text{S}\)) and become less susceptible to bacterial remineralization (SI), in a process known as “sulfurization”\textsuperscript{29}.

Because the time-scale of warming leading up to the P/Tr boundary is slow relative to the adjustment time-scale of large-scale ocean circulation (i.e. warming likely occurred over \(\sim39\) kyr or more, starting in the *C. meishanensis* biostratigraphic zone\textsuperscript{6,11}), a series of (10 kyr) steady-state simulations is appropriate for simulating the biogeochemical response to warming. In these, we prescribe a range of atmospheric \(p\text{CO}_2\) (1 – 30 \(\times\) pre-industrial \(p\text{CO}_2\), i.e. 280–8400 ppmv) chosen to span the increase in tropical Tethys ocean temperatures reconstructed from proxy records (\(\sim22 – 35^\circ\text{C}\), Fig. 1a+d, SI). Simultaneously, we explore the importance of 1 – 2.5\(\times\) modern ocean
phosphate inventories to represent the potential net impact of increased weathering and sediment
regeneration rates as the climate warms and ocean anoxia increases, respectively\textsuperscript{30–32} – thus, creat-
ing model ensembles of varying climate vs. ocean nutrient state. Atmospheric oxygen is fixed at
modern.

Constraining model results with global and local redox proxies

Uranium isotopes can provide powerful constraints on ocean models via the reconstructed extent
of seafloor anoxia (f\textsubscript{anox}). To quantitatively compare the ESM results with a compilation of car-
bonate $\delta^{238}$U data over the P/Tr transition (SI), we use a forward box model that encapsulates the
uncertainties in the U isotope budget (adapted from Lau et al.\textsuperscript{9}). According to our U-model results,
the $\delta^{238}$U data can be best explained by an abrupt increase in f\textsubscript{anox} that either coincided with the
EH, or preceded it by much less than the onset of the warming event (Fig. 1 b+c). An increase
of f\textsubscript{anox} from a modern value of 0.6\% to about 30\% (i.e. a factor of 50) represents our preferred
scenario as other perturbations fail to simulate the rate of change and magnitude of the shift in the
$\delta^{238}$U data (Extended Data Fig. 4).

We also ground-truth the ESM results with a new compilation of local redox proxies (Ex-
tended Data Fig. 1 and Extended Data Table 2). The data-set consists of geochemical, lithologic,
sedimentologic, and biomarker evidence for water-column euxinia and bottom water anoxia and
distinguishes three phases of the P/Tr transition (Late Permian background, Start Warming and
Main Extinction, Extended Data Table 2). The Late Permian data only indicate photic-zone eu-
xinia occurring at the Meishan section with no clear evidence for seafloor anoxia (Fig. 3a+g,
Extended Data Table 2). Immediately before the EH, water-column euxinia expanded to sections in British Columbia (BC), Shangsi, and potentially to the equatorial Panthalassic (Japan), while unequivocal evidence for bottom water anoxia remains limited and only exists for BC (Fig. 3b+h). In contrast, during the Main Extinction, anoxia spread across much of the shallow seafloor, and multiple lines of evidence suggest widespread euxinia impinged on shallow marine habitats (Fig. 3c+i).

**Impact of temperature-driven respiration on the marine redox-landscape**

Our model experiments show that for a 'static' biological pump, global POM cycling (i.e. POM export production, rain and burial rates within the sediment) is almost entirely controlled by PO$_4$ availability, with a minor increase at higher temperatures attributable to temperature-dependent productivity (Fig. 2a–c). Global mean photic-zone [H$_2$S] shows little temperature sensitivity and remains below 4 µmol kg$^{-1}$ (Fig. 2d) and the depth of maximum [H$_2$S] is generally below 400m (Extended Data Fig. 7). At the same time, the extent of seafloor anoxia increases to values above 30% even at moderately high warming and nutrient increases (Fig. 2e). The relative lack of sensitivity of shallow euxinia vs. deep anoxia cannot easily be reconciled with observations for photic-zone euxinia (Extended Data Fig. 7) and expanded seafloor anoxia (Fig. 1b+c), respectively.

In contrast, a temperature-dependent biological pump results in more efficient POM remineralization and nutrient recycling in the upper ocean, which significantly enhances export production (2f, and Extended Data Fig. 5a–d). This positive feedback is further intensified by the assumed
slower-than-modern sinking rate in the Paleozoic\textsuperscript{23} (Extended Data Fig. 5c), as it increases the residence time of POM in the upper ocean, leading to more complete remineralization and nutrient recycling. Although POM export production increases by up to a factor of three compared to the static model, the POM rain to the sediments does not change significantly (Fig. 2g) due to the temperature driven, efficient POM remineralization in the water column. Mean photic-zone [H\textsubscript{2}S] is substantially higher (reaching values > 60\(\mu\)mol kg\(^{-1}\)) and highly sensitive to temperature variations (Fig. 2i). Notably, higher temperatures cause an increase in upper ocean [H\textsubscript{2}S] and a concomitant shallowing of the chemocline – even without the need to invoke any change in nutrient inventory (Extended Data Fig. 8). In addition, increased ocean euxinia leads to higher sulfurization rates causing POM burial rates to increase (Fig. 2h) and the extent of seafloor anoxia to decrease (compare Fig. 2j+e; S6), a negative feedback that may be important in the transition back to a more oxygenated ocean\textsuperscript{33}.

Our model predictions for the spatial distribution of euxinia and seafloor anoxia appear in general agreement with the available evidence for local redox-conditions (Fig. 3) and our U-model results (Fig. 1b+c). In our “Late Permian background” scenario (i.e. lower temperatures and modern ocean [PO\textsubscript{4}]), only a few very local environments developed [H\textsubscript{2}S] around 20–30\(\mu\)mol/kg and are limited to depths below 284m (Fig. 3a+d), similar to profiles in the modern Cariaco Basin\textsuperscript{34}. Instances of upper ocean euxinia were very limited in spatial extent and only occurred in the Eastern Equatorial Panthalassic and the Eastern Tethys (South China). The simulated extent of bottom water anoxia, 0.7% of the seafloor, is comparable to the modern value of 0.6% (\textsuperscript{35}, Fig. 3g). Consistent with proxy reconstructions, climate warming together with a moderate release
of nutrients (i.e. the “Start Warming” phase), resulted in increasing [H$_2$S], with sulphidic waters impinging onto continental shelves and slopes, especially in warm equatorial waters (Fig. 3b+e).

While most of the global seafloor remains oxic ($f_{\text{anox}} = 1.7\%$), approximately 20% of the seafloor shallower than 1000m exhibits [$O_2] < 60\mu\text{mol/kg}$ (Fig. 3h, Extended Data Table 4), a typical threshold for hypoxic conditions and considered critical for the survival of many modern marine animals$^{22}$. A second increase in temperature together with another slight relaxation of nutrient-limitation (i.e. a $\sim 7^\circ\text{C}$ warming of SSTs and a doubling of ocean [PO$_4$] compared to modern) is sufficient to simulate the “Main Extinction”. This scenario satisfies not only local evidence for an expansion of upper ocean euxinia (Fig. 3c) but also predicts more widespread seafloor anoxia that has spread to the abyssal plain (Fig. 3i), in broad agreement with inferences from $\delta^{238}\text{U}$ data (Fig. 1b+c). The habitable area in the upper ocean is further restricted as now $\sim 30\%$ of the seafloor above 1000m exhibits hypoxic conditions (Extended Data Table 4).

**Implications for ocean-redox and carbon cycle dynamics**

Given the relatively prolonged interval of warming in the lead up to the P/Tr boundary ($\sim 39 \text{ kyr}^6$), our analysis favors a conceptual model in which higher metabolic rates drive a pronounced vertical partitioning in ocean redox. This biogeochemically driven partitioning occurs within an ocean that remains not only well ventilated at depth, but consistent with previous modelling work$^{13,36}$, increases in overturning strength for warmer states (Figure 3j-l). The temperature impact on metabolic rates alone is hence sufficient to provide an effective kill mechanism for the upper ocean ecosystem. This is in contrast with a physical partitioning such as simulated by Penn et al.$^{12}$ using the Community Earth System Model (CESM), whereby instantaneous warming drives
persistent (multi kyr) stratification of the ocean. These two conceptual (and numerical) models also fundamentally differ in the consequent predictions of biological export – vigorous circulation, in conjunction with temperature-driven nutrient recycling substantially enhances export, whereas stratification severely restricts upwelling and hence export – with important implications for the stressors associated with the marine extinction. Given that the initial ocean circulation response of the cGENIE ESM to instantaneous warming is very similar to that of CESM immediately after the perturbation (Extended Data Fig. 10), it is clear how critical the time-scale of warming is to fully understand the mechanistic link between anoxia and the extinction, highlighting the importance of further work in refining age models and temperature reconstructions for the latest Permian.

Our inference of a metabolically-driven – rather than transient circulation-driven redox partitioning, allows for persistently high temperatures during the Early Triassic\(^4\) to prolong the occurrence of extensive seafloor anoxia\(^9\). Episodic volcanism in the Early Triassic\(^37\) and consequent oscillations between sulfidic and oxic conditions potentially played a role in the protracted biogeochemical and biological recovery prior to the Middle Triassic. Our finding that the temperature response of nutrient recycling and ocean redox is somewhat amplified in the model under a slower POM sinking rate also implies that the severity of marine extinction should decrease through the Phanerozoic. Specifically, the advent of pelagic biomineralization in the early Mesozoic Marine Revolution\(^38\), leading to a step-increase in POM sinking rates\(^23\), may have decreased the sensitivity of ocean anoxia to fluctuations in global climate and hence volcanism-related carbon release in the latter half of the Phanerozoic\(^39\).
Finally, our numerical model analysis sheds new light on the $\delta^{13}C$ decline itself, and specifically the cause for substantive variability in what is nominally a globally imprinted signal. Differences in onset timing, temporal evolution, and maximum isotopic change of the end-Permian $\delta^{13}C$ decline have been observed among stratigraphic sections\(^\text{10}\) (e.g. the amplitude varies between 4 and 7\(\%\)), complicating estimates of the size and source of the carbon cycle perturbation.

We simulate a maximum decrease in the Tethys Ocean subsurface $\delta^{13}C$ during the P/Tr of 3.9\(\%\) – approximately 60\(\%\) of the observed $\delta^{13}C$ decrease in Armenia and Iran, with a smaller shift occurring in colder waters (Fig. 1e). This decline is driven only by temperature-induced changes to the biological pump in the model without invoking changes in the ocean+atmosphere carbon inventory (see SI). The implication is that end-Permian carbon release as inferred from observed $\delta^{13}C$ changes (e.g. Erwin\(^3\)) is likely overestimated, with the total release being smaller and/or the isotopic composition of the source is less negative, than previously assumed. This implies that carbon from volcanism rather than a reduced source (e.g. organic matter) was more dominant. In sum, these results reassess the relationship between temperature and the ocean redox state, and carbon cycle perturbations recorded by $\delta^{13}C$. 


Figure 1: **Temporal relationship of changes in isotope records and U mass balance modeling for the P/Tr extinction.** (a) Temperature reconstructions from the $\delta^{18}O$ of biogenic apatite from South China (black circles)$^4$. (b) Carbonate $\delta^{238}U$ data (colored symbols)$^9,17,40–42$. U isotope forward model results are shown, with gray lines representing individual iterations from the Monte Carlo routine with variable isotopic fractionation into anoxic sediments, riverine $\delta^{238}U$, and carbonate diagenetic offset. The black line represents the moving average of all model runs (SI). (c) Varying perturbations in seafloor anoxic fraction ($f_{\text{anox}}$) that drive the U-model in panel b (individual iterations, grey lines; average, black line). (d + e) Conodont apatite $\delta^{18}O$ and $\delta^{13}C$$^6,43$ (SI). Grey shading in (e) represents the range of cGENIE $\delta^{13}C$ values simulated for the Tethys Ocean for the experiments shown in Fig. 3.
Figure 2: **Global sensitivity of particulate organic matter (POM) cycling and ocean redox to temperature and nutrient changes** for the static and dynamic representation of the biological pump: POM flux values (in PgC yr$^{-1}$) of export production (a+f), POM rain to the seafloor (b+g) and POM burial in the sediments (c+h). Mean photic-zone [H$_2$S] (in $\mu$mol kg$^{-1}$, d+i) and bottom water anoxia (e+j) as fraction of seafloor area with [O$_2$] $\leq$ 5$\mu$mol kg$^{-1}$ (in %). The red diamonds indicate results for the experiments presented in Fig. 3.
Figure 3: **Ocean redox conditions during the P/Tr transition using the dynamic cGENIE model:** (a-c): Simulated maximum [H$_2$S] between 81 and 928m. (d-f): Depth where the maximum in [H$_2$S] is observed. (g-i): Simulated extent of seafloor anoxia (values indicate f$_{anox}$). Model results for [H$_2$S] and [O$_2$] are superimposed by proxy observations: Evidence for euxinia/anoxia is represented by circles; evidence against by crosses; ambiguous evidence or dynamic redox-conditions by triangles (see Extended Data Table 2). (j-l): Meridional overturning circulation (MOC, in Sv).
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Competing Interests  The authors declare no competing interests.

Supplementary Information  is available for this paper.

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Data availability
The locations of all data used in this study are provided in the supplementary information.

Code availability
The version of the code used in this paper is tagged as release v0.9.15 and has a DOI of 10.5281/zenodo.4008865. Necessary boundary condition files are included as part of the code release. Configuration files for the specific experiments presented in the paper can be found in the installation subdirectory: genie-userconfigs/MS/huelseetal.2020. Details of the experiments, plus the command line needed to run each one, are given in the readme.txt file in that directory. A man-
ual describing code installation, basic model configuration, and an extensive series of tutorials is provided. The Latex source of the manual and pre-built PDF file can be obtained by cloning (https://github.com/derpycode/muffindoc).