Title: Ocean Acidification and the Permo-Triassic Mass Extinction

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Abstract: Ocean acidification triggered by Siberian Trap volcanism has been implicated as a kill mechanism for the Permo-Triassic mass extinction, but evidence for an acidification event remains inconclusive. To address this, we present a high resolution seawater pH record across this interval, utilizing boron isotope data combined with a quantitative modeling approach. In the latest Permian, the alkalinity of the ocean increased, priming the Earth system with a low level of atmospheric CO₂ and a high ocean buffering capacity. The first phase of extinction was
coincident with a slow injection of isotopically light carbon into the atmosphere-ocean, but the
ocean was well-buffered such that ocean pH remained stable. During the second extinction pulse,
however, a rapid and large injection of carbon overwhelmed the buffering capacity of the ocean,
causing an abrupt and short-lived acidification event that drove the preferential loss of heavily
calcified marine biota.

One Sentence Summary: Ocean acidification caused the second phase of mass extinction in the
Permo-Triassic, due to a rapid and large injection of carbon which overwhelmed the buffering
capacity of the ocean.

Main Text: The Permian Triassic Boundary (PTB) mass extinction, at ~ 252 Ma, represents the
most catastrophic loss of biodiversity in geological history, and played a major role in dictating
the subsequent evolution of modern ecosystems (1). The end-Permian extinction event spans ~60
kyrs (2) and can be resolved into two distinct marine extinction pulses, with the respective kill
mechanisms appearing to be ecologically selective (3). The first occurred in the latest Permian
(Extinction Pulse 1; EP1) and was followed by an interval of temporary recovery before the
second pulse (EP2) which occurred in the earliest Triassic. The direct cause of the mass
extinction is widely debated with a diverse range of overlapping mechanisms proposed,
including widespread water column anoxia (4), euxinia (5), global warming (6) and ocean
acidification (7).

Models of PTB ocean acidification suggest that a massive, and rapid, release of CO₂ from
Siberian Trap volcanism, acidified the ocean (7). Indirect evidence for acidification comes from
the interpretation of faunal turnover records (3, 8), potential dissolution surfaces (9) and Ca
isotope data (7). A rapid input of carbon is also potentially recorded in the negative carbon isotope excursion (CIE) that characterizes the PTB (10, 11). The interpretation of these records is, however, debated (12), and of great importance to understanding the current threat of anthropogenically-driven ocean acidification (11).

Here, we test the ocean acidification hypothesis by presenting a novel proxy record of ocean pH across the PTB, using the boron isotope composition of marine carbonates ($\delta^{11}$B$_{\text{carb}}$) (SM sections 2 to 4). We then employ a carbon cycle model (SM sections 3 to 5) to explore ocean carbonate chemistry and pH scenarios that are consistent with our $\delta^{11}$B data and published records of carbon cycle disturbance and environmental conditions. The quantitative model uses previous estimates for background Early Permian conditions (13) suggesting either high $p$CO$_2$ ($CO_2$Hi: ~10 PAL, pH ~7.5 $\delta^{11}$B$_{\text{SW}}$ ~36.8‰), or low $p$CO$_2$ ($CO_2$Lo: ~3 PAL, pH ~8, $\delta^{11}$B$_{\text{SW}}$ ~34‰) (see SM sections 5 and 6 for further details). Through this combined geochemical, geological and modelling approach we are able to produce an envelope that encompasses the most realistic range in pH, which then allows us to resolve three distinct chronological phases of carbon cycle perturbation, each with very different environmental consequences for the Late Permian-Early Triassic Earth system.
We analyzed boron isotope data from two complementary transects in a shallow marine, open water carbonate succession from the United Arab Emirates (U.A.E.), where depositional facies and δ^{13}C_{carb} are well constrained (14) (see SM sections 1 and 2). During the Permian-Triassic the U.A.E formed an expansive carbonate platform that remained connected to the central Neo-Tethyan Ocean (15) (Fig 1). The run-up to PTB in the Tethys is characterized by two negative δ^{13}C excursions interrupted by a short-term positive event (10). There is no consensus as to the cause of this rebound event and so we focus on the broader δ^{13}C trend. Our δ^{13}C transect (Fig. 2) starts in the Changhsingian with a gradual decreasing trend, interrupted by the first negative shift in δ^{13}C at EP1 (at 53 m or ~251.96 Ma, Fig. 2). This is followed by the minor positive ‘rebound’ event (at 54 m or ~251.95 Ma, Fig. 2) prior to the minima of the second phase of the negative CIE (58-60 m or ~251.92 Ma, Figs. 2 and 3) that marks the PTB itself. After the CIE minimum, δ^{13}C gradually increases to ~1.8‰ and remains relatively stable during earliest Triassic and across EP2.

Our boron isotope transect shows a quite different pattern. δ^{11}B is persistently low (Fig. 2), at the start of our record during the late-Changhsingian (Late Permian), with an average of 10.9 ± 0.9‰ (1σ). This is in agreement with δ^{11}B values (average of 10.6 ± 0.6‰, 1σ) reported for early-Permian brachiopods (16). Further up section (at ~40 m or ~252.04 Ma, Fig. 2), there is a stepped increase in δ^{11}B to 15.3‰, and by implication an increase in ocean pH of ~0.4-0.5 pH units (Fig. 3). Then δ^{11}B values remain relatively stable, scattering around 14.8‰ (± 1.0, 1σ) and implying variations within 0.1-0.2 pH units, into the Early Griesbachian (Early Triassic) and hence across EP1 and the period of carbon cycle disturbance (Figs. 2 and 3).

After δ^{13}C had increased and stabilized (at ~85 m or ~251.88 Ma, Fig. 2), δ^{11}B begins to decrease rapidly to 8.2‰, implying a sharp drop in pH of ~0.6-0.7 pH units. The δ^{11}B minimum
is coincident with the interval identified as EP2. This ocean acidification event is short-lived (~10 kyrs) and δ¹¹B values quickly recover toward the more alkaline values evident during EP1 (average of ~14‰).

The initial rise in ocean pH of ~0.4-0.5 units during the Late Permian (Fig. 3) suggests a large increase in carbonate alkalinity (17). We are able to simulate the observed rise in δ¹¹B and pH through different model combinations of increasing silicate weathering, increased pyrite deposition (18), an increase in carbonate weathering and a decrease in shallow marine carbonate depositional area (see SM section 6.1). Both silicate weathering and pyrite deposition result in a large drop in pCO₂ (and temperature) for a given increase in pH and saturation state (Ω). There is no evidence for a large drop in pCO₂, and independent proxy data indicate only a minor temperature decrease of a few degrees C during the Chansingian (19), suggesting that these mechanisms alone cannot explain the pH increase (see sensitivity tests in SM section 6.1).
Conversely, an increase in carbonate input or a reduction in rates of carbonate deposition both result in increases in $\Omega$, with a greater impact on pH per unit decrease in $pCO_2$ and temperature (see Fig. S6).

This suggested decrease in carbonate sedimentation is consistent with the decrease in depositional shelf area that occurred due to the 2nd order regression of the Late Permian (20). With the added expansion of anoxia into shelf environments (21) this would effectively create both bottom-up and top-down pressures to reduce the area of potential carbonate sedimentation. Sea level fall also exposed carbonates to weathering (20), which would have further augmented the alkalinity influx. The pH increase event supports the CO$_2$Lo initialisation scenario (CO$_2$ ~3 PAL, pH ~8, $\delta^{11}$B$_{SW}$ ~34‰) as the simulated CO$_2$ and temperature decrease is much reduced, and therefore more consistent with independent proxy data (22), compared to CO$_2$Hi (CO$_2$ ~10 PAL, pH ~7.5 $\delta^{11}$B$_{SW}$ ~36.8‰) (Fig. 3D).

Prior to EP1, $\delta^{13}$C$_{carb}$ values begin to decrease before reaching the minimum of the globally recognized negative CIE at the PTB (Fig. 2). At this time both $\delta^{11}$B and ocean pH remained stable. Hypotheses to explain the negative CIE require the input of isotopically light carbon, such as from volcanism (14, 23) with the assimilation of very light organic carbon from the surrounding host rock (24), methane destabilization (22), collapse of the biological pump (15), and/or a decrease in the burial of terrestrial carbon (16). We can simulate the observed drop in $\delta^{13}$C$_{carb}$, whilst remaining within the uncertainty of the $\delta^{14}$B data (Fig. 3), by combining a cessation of terrestrial carbon burial with a relatively slow (50 kyr) carbon injection from any of the above sources (see section S6.2.4, Fig S8). A small source of methane (3.2 $\times$10$^{17}$ mol C with $\delta^{13}$C = -50‰) gives the least change in $\delta^{11}$B and pH, whilst either a larger source of organic
carbon (~6.5x10^{17} mol C with δ^{13}C = -25‰) or a mixture of mantle and lighter carbon sources
(~1.3x10^{18} mol C with δ^{13}C = -12.5‰) are still within the measured uncertainty in δ^{11}B.

This relatively slow carbon addition minimises the tendency for a transient decline in
surface ocean pH in an ocean that was already primed with a high Ω and hence high buffering
capacity from the Late Permian. The global presence of microbial and abiotic carbonate fabrics
after EP1 (Fig. 2) (25) are indicative that this high Ω was maintained across the CIE. The carbon
injection triggers an increase in pCO₂, temperature and silicate weathering, thereby creating an
additional counterbalancing alkalinity flux. This is consistent with independent proxy data (6).
The alkalinity source may have been further increased through soil loss (26), the emplacement of
easily-weathered Siberian Trap basalt, or the impact of acid rain (27) that would have increased
weathering efficiency.

The negative δ^{11}B_{carb} excursion at 251.88 Ma represents a calculated pH decrease of up to
0.7 pH units. It coincides with the second pulse of the extinction (Fig. 2), which preferentially
affected the heavily calcifying, physiologically un-buffered and sessile organisms (3). This was
also accompanied by the temporary loss of abiotic and microbial carbonates throughout the
Tethys (28, 29) thereby suggesting a coeval decrease in Ω (30). To overwhelm the buffering
capacity of the ocean and decrease pH in this way requires a second, more abrupt injection of
carbon to the atmosphere, yet remarkably, the acidification event occurs after the decline in δ^{13}C,
when δ^{13}C has rebounded somewhat and is essentially stable (Fig. 2).

Unlike the first carbon injection, the lack of change in δ^{13}C at this time rules out very
^{13}C-depleted carbon sources, because no counterbalancing strongly ^{13}C-enriched source exists.
Instead, it requires a carbon source near ~0‰. A plausible scenario for this is the decarbonation
of overlying carbonate host rock, into which the Siberian Traps intruded (24) or the direct
assimilation of carbonates and evaporites into the melt (31). Host carbonates would have had δ¹³C ~+2-4‰, which when mixed with mantle carbon (~+5‰), potentially produces a source near 0‰. We can simulate the sharp drop in pH and stable δ¹³C values (Fig. 3) through a large and rapid carbon release of 2×10¹⁸ mol C over 10 kyr (Fig S8). This second rapid carbon release produces a sharp rise in pCO₂ to ~20 PAL and warming of ~15°C, consistent with the observation of peak temperatures after EP1 (26). Initialization of the carbon cycle model under CO₂Hi cannot generate the magnitude of δ¹¹B drop (Fig. 3A) because the non-linear relation between pH and δ¹¹B fractionation sets a lower limit of δ¹¹B at ~10‰ in this case (Fig. S3). Thus low initial CO₂ of ~3 PAL in the late Permian (CO₂Lo) is more consistent with the data presented here.

The documented acidification event lasted for only ~10 kyrs. This time span is consistent with the modelled timescale required to replenish the ocean with alkalinity, as carbonate deposition is reduced and weathering is increased under higher pCO₂ and global temperatures. Increased silicate weathering rates drive further CO₂ drawdown resulting in stabilization (Fig. S7). High global temperature (6) and increased silicate weathering are consistent with a sudden increase in both ⁸⁷Sr/⁸⁶Sr (32) and sedimentation rates (26) in the Griesbachian.

The Permo-Triassic transition was a time of extreme environmental change, and our combined data and modeling approach falsifies several mechanisms for the changes observed. Whilst the coincident stresses of anoxia, increasing temperatures, and ecosystem restructuring were important during this interval, the δ¹¹B excursion strongly suggests that widespread ocean acidification was the driver of the second pulse of the mass extinction, and thus ultimately ended the temporary recovery (3) from the first extinction pulse. The carbon release required to drive the observed acidification event occurred at a rate comparable to the current anthropogenic
perturbation, but far exceeded it in expected magnitude (33). We show that such a rapid rate is
critical to causing the combined synchronous decrease in both pH and saturation state that
defines an ocean acidification event (11).
References and Notes


17. the alternative way to drive an increase in pH would be through a removal of carbon, however this would be evident in the $\delta^{13}$C record so we can rule it out.

18. Bacterial Sulfate Reduction (BSR) is a net source of alkalinity if the generated H$_2$S is buried as pyrite. Pyrite deposition is seen widely in certain setting during the Late Permian to PTB. See SI for further information.


30. Note that the system cannot be undersaturated as this precludes the preservation of the boron isotope record.


33. The imposed perturbation for the acidification event is 24000 PgC compared to the estimates of 4-5000PgC that could be generated from conventional fossil fuels. Upper estimates using unconventional fossil fuels (e.g. methane hydrates) can reach ~ 24000 PgC.


78. Y. Cui, L. R. Kump, Global warming and the end-Permian extinction event: Proxy and modeling perspectives. (2014); (doi:10.1016/j.earscirev.2014.04.007).


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Fig. 1: Paleogeographic reconstruction for the Late Permian denoting the studied section Wadi Bih, in the Musandam Mountians of U.A.E that formed an extensive carbonate platform in the Neo-Tethyan Ocean. Modified from (14).

Fig. 2: Carbon cycle dynamics, macrofauna distribution (34), and Extinction Phase 1 (EP1) and Extinction Phase 2 interval (EP2) across the Permian Triassic Boundary for Wadi Bih, A: shallow water δ¹³C record (14); B: Boron isotope (δ¹¹B) record (propagated uncertainty given as 2σf) and average Early Permian brachiopod value (n=5) (16). Blue symbols are for SHA1 transect, black symbols are for WSA transect. The two transects are separated by ~1km and facies are laterally continuous. Only H. parvus has been found so far in this section and the conodont zones with dashed line are identified from the δ¹³C record (34-36).

Fig. 3: Model results of carbon cycle parameters for the two end-member CO₂ scenarios (CO₂Hi and CO₂Lo). A - Model reproduced δ¹¹B vs data. B – Modeled δ¹³C vs data. C – Modeled pH
envelope incorporating uncertainty of $\delta^{11}B_{SW}$ and dynamic temperatures. D – calculated atmospheric CO$_2$. See SM section 1.2 for details on age model.
Supplementary Materials

1. Materials and Methods

1.1 Sample Section

Carbonate samples were obtained from a shallow-marine platform section at Wadi Bih on the Musandam Peninsula, United Arab Emirates (UAE). GPS co-ordinate for main transect in Wadi Shahha are N 025° 50' 31.7", E 056° 06' 41.7". This is a near-continuous and exclusively shallow marine carbonate succession from the late Permian and entire Early Triassic that allows analysis of a high-resolution signature in the absence of significant depth-dependent or lithological controls (14). Late Permian facies are predominantly intertidal mud-and-wackestones and open lagoon wackestones, occasional windward and leeward shoals of bioclastic pack-and-grainstones (34). The PTB and Early Triassic are regionally represented by ooidal grainstones and a thrombolite horizon (14, 34). Samples were taken from two transects Wadi Shahha (WSA) and Sha (SHA1), ~1000 m apart. Facies are laterally continuous and carbon isotopes were used to ensure careful integration of the two datasets. For this study, we have analyzed 25 carbonate samples in total, taken in approximately 1 to 10 m scale intervals and covering a total thickness of 98 m, starting in the mid-Changhsingian (Permian), going up into the mid-Griesbachian (Triassic) and bracketing the complete Permian Triassic Boundary (PTB) extinction event (Table S1).
1.2 Age Model

The age model for this study was based on the most recent findings of Burgess et al., (2) (see Table S1). The age tie points are 252.10 Ma for 20 m (Fig. 2) thought to be equivalent to Bed 22 in Meishan from the δ^{13}C record; 252.00 Ma for the decline in δ^{13}C at 49 m and 251.90 Ma for the first occurrence of *H. parvus* at 61 m. EP2 is known to occur at the end of the *I. staeschi* zone, Bed 28 Meishan (3), which is not recorded in the Neo-Tethys but is equivalent to the carbon

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* Ages are calculated based on tie points from Burgess et al.(2), see section S1.2
* *external uncertainty for B isotope data are valid for the last digits (2ı)
* *propagated uncertainties for B isotope data

Table S1: Boron, carbon and oxygen isotope data from Wadi Bih; U.A.E.; pH values are derived from a simplified and non-dynamic calculation using the δ^{11}B_{SW} range given by the model calculation and a constant pK_{B} for 25°C, 35 psu, 0 dbar.
isotope rise between the *H. Parvus* and *I. isarcica* zones. In Wadi Bih we see the loss of gastropods and bivalves at this point (34), however the full resolution of the second extinction phase has not been confirmed at this locality. Therefore we identify a 10 m interval for EP2. In order to complete the age model we set the mid-point of EP2 as 251.88 Ma based on the absolute age for EP2 in Meishan (2).

1.3 Analytical methods

Carbon and oxygen isotope ratios were determined at Edinburgh University and University of Graz using the preparation technique and measurement routine as detailed in (19). All carbonate isotopic values are quoted in the conventional δ per mil (‰) notation relative to VPDB. Calibration to international reference material was through NBS 19 and the reproducibility of replicate analyses for reference material, standards (in-house) and carbonate samples was better than ±0.05 ‰ for δ13C and ±0.1 ‰ for δ18O at one standard deviation. For a detailed discussion of the C and O isotopic data see (19).

Boron isotope ratios were determined in the isotope geochemistry laboratory at the University of Bremen (Department of Geosciences and MARUM-Center for Marine Environmental Sciences) using a ThermoFisher Scientific TRITON Plus Thermal Ionization Mass Spectrometer. The n(11B)/n(10B) measurements were performed using negative thermal ionization mass spectrometry (N-TIMS) following the method detailed in (37). For analyses, 10 mg of the sample powder was dissolved in 100 μl 1 N HCl for 24 h at 20°C and subsequently centrifuged. 1 μl boron-free seawater emitter (38) together with 1 μl of the sample solution containing ~1 ng B were placed and dried on a degassed Re single filament. Analyses were carried out at filament temperatures of 970°C-1050°C. Boron isotopes were registered as BO2−.
complexes on masses 42 and 43, and measurements were carried out at ion beam intensity of ~
10 pA on mass 43. Each sample measurement involved up to 200 blocks with 10 cycles each,
taking about 2 hours of data acquisition. B isotope ratios are given relative to NIST SRM 951 in
the conventional $\delta^{11}\text{B} (\text{‰})$ notation. The external reproducibility of the certified reference
material NIST SRM 951 showed an $n(^{11}\text{B})/n(^{10}\text{B})$ ratio of 4.0065±0.0017 ($2\sigma = 0.42\text{‰}$, n=23)
over a period of 6 month of sample analyses. The long term (18 month) reproducibility is
4.0066±0.0018 ($2\sigma = 0.44\text{‰}$, n=58). The $n(^{11}\text{B})/n(^{10}\text{B})$ ratio of the reference material for each
analytical session was reproduced better than 0.6‰ ($2\sigma$). In addition to the NIST material, the
standard material M93-TB-FC-1, a Porites coral with a published value of 24.8±0.4‰ ($2\sigma_{\text{mean}}$),
as determined by different multicollector techniques (39) was also regularly analysed. The coral
replicates gave $\delta^{11}\text{B}$ values of 24.1±0.7‰ ($2\sigma$, n=16). Each sample solution was as a minimum
run in full duplicate and the uncertainty of the reference material was propagated into the
external uncertainty ($2\sigma$) on the isotope ratio of the sample ($2\sigma_f$; Table S1). For further
information on the preparation and analytical methods see (40).

2. Sample Selection

A critical issue in using the B isotope composition of Permo-Triassic carbonate rocks for
reconstruction of ocean pH is the potential overprinting of the original isotope signal via
alteration. To obtain high-quality samples in which primary B isotope signals are still preserved,
we applied the sample selection procedures successfully used on Neoproterozoic carbonate rocks
to reconstruct Cryogenian and Ediacaran ocean pH variation (37, 40, 41). In brief, samples
selected for isotope analyses were screened macroscopic (in the field), microscopic (scanning
electron microscope) and geochemically (carbon and oxygen isotopes), and selected because of
their uniformity in texture, absence of late stage secondary alteration and no correlation between carbon and boron with oxygen isotopic signatures (Figs. S1 and S2).

The PTB interval itself was thought to occur in a regional cross-bedded ooid grainstone, however, reconsideration of published thin-section images (34) (Fig S1 samples from WSA transect, 0611300847 and 0611181243) demonstrate these are in fact microspheres (a.k.a calcispheres). This fabric is unusual for the Phanerozoic but appears to represent supersaturated conditions and these are thought to be primary spar precipitates (42).

To gain the highest potential for recording a primary boron signature we microdrilled areas of pure micrite from micrite mudstones and micritised calcisphere grainstones where there was no micro-optical evidence for veining, fracturing, clay minerals or bioclastic material. Samples containing evidence of late stage secondary alteration or recrystallization, i.e. any spar/microspar, were discarded. Potential analyses of disseminated detrital material in the carbonates was also checked through elevated Al, Si and Ba concentrations and showed either no or only minor dissemination of clay. The low availability of bioclastic material in this interval, due to the extinction, argues against the potential of trends being caused by vital effects. In particular the calcisphere grainstones of the PTB interval are classed as an abiotic carbonate that provides an excellent opportunity to record seawater $\delta^{11}$B in the absence of vital effects.
Fig S1: Examples of thin section images for the Wadi Bih section, WSA transect. WSA samples demonstrate homogeneous micritic texture of samples used for $\delta^{11}$B analysis. 06- samples are from Maurer et al., illustrating grainstones. The lack of compaction of grains and pore filling equant spar cements indicate very early/syn-sedimentary cementation. This fabric is consistent with indicators for supersaturated conditions in this interval, including thrombolites and flat pebble conglomerates, and suggests preservation of the original depositional fabric. Sample heights (m) as in Fig. 2 and Table S1.
Fig S2: Cross-plots of boron, carbon, and oxygen isotope data for the marine carbonate samples from the Wadi Bih section. No significant correlation can be observed.

2.1 Diagenetic Influences

The PTB interval grainstone is composed of microspheres (a.k.a calcispheres). Microspheres are micritized and cemented with coarse equant spar cement (Fig S1). The lack of compaction of the microspheres suggests that the spar cement was extremely early and probably syn-sedimentary. This is a feature of other grainstones throughout this interval (WSA transect, sample 0611301104). Critically the presence of such well cemented fabrics in the grainstones of this interval would have prevented later stage fluid migration, and hence any late stage dolomitization. The total negative boron isotope excursion at EP2 is recorded across a number of fabrics and facies, including micrite and the early cemented grainstones. Petrographic analysis
shows the extreme of the acidification event is recorded in fine-grained micrite where textures are very homogenous samples WSA 1, 1B, 2, and 2A (Fig. S1).

Dolomitization in the Wadi Bih section is observed (14), and occurred in two phases where the first phase was fabric retentive syn-sedimentary dolomitization. The second phase of dolomitization leads to the recrystallization of facies where near depositional porosity and permeability had been maintained, i.e. preferentially in non-cemented grainstones. Neither of these phases is classed as deep burial dolomitization (as confirmed by petrography in Figure S1 and the δ18O data, Table S1). In the Musandam Peninsula the impact of dolomitization on carbon and oxygen isotopes can be seen only in the close proximity to regional faults that provided high permeability pathways for late burial dolomitizing fluids (43), which were avoided for this study.

Diagenetic effects were also checked with geochemical tests for selected trace element analyses, using secondary ionisation mass spectrometer Cameca ims 4f at the University of Edinburgh. Diagenetic alteration was explored via Mn/Sr, which is often used as a geochemical indicator of alteration and meteoric diagenesis in ancient carbonates (44). While low Mn/Sr has been found in ancient carbonates where there is clear optical evidence for recrystallization (45), high Mn/Sr may indicate carbonate precipitation from anoxic waters. In the selected samples, Mn concentration is < 300 μg g⁻¹, Sr concentration ranges from 140 to 1400 μg g⁻¹, and the Mn/Sr ratio is low (< 2), so suggesting no influence of meteoric fluids. The boron concentration for the carbonate rocks is, on average, 1 μg g⁻¹ and ranges between 0.2 and 1.7 μg g⁻¹.

Post-depositional alteration, especially meteoric diagenesis and recrystallization, is assumed to decrease the isotopic composition of oxygen, boron and carbon isotopes (e.g. 46-48). Our selected carbonate samples show the distinct carbon isotope trend found at every PTB section globally and δ18O values ranging between -0.5 and -4.0‰, indicating no significant deep
burial alteration. All carbon and oxygen isotope data are given in Table S1. No statistically significant correlation between carbon, oxygen and boron isotope data can be observed in our data (Fig. S2).

The replication of the $\delta^{11}$B across two complementary transects further support the preservation of a primary seawater isotope signature as late stage dolomitization is expected to be highly laterally variable and disrupt the smooth trends seen in the data.

3. Support for a primary Boron isotope signature

3.1 Published $\delta^{11}$B data

So far, $\delta^{11}$B data for Triassic carbonates have not been published and only limited $\delta^{11}$B data, based on low-Mg calcite brachiopod calcite from Oman (Saiwan Fm.), are available for the Permian (Late Sakmarian). Keeping in mind the modern residence time of boron ($T \sim$14 to 20 Ma (47, 49), it is important to note that the range in $\delta^{11}$B values ($10.9 \pm 0.9\%$ (1$\sigma$, $n=4$), 252.05-252.15 Ma, mid-Changhsingian) overlap with the range in $\delta^{11}$B values between 10.1 and 11.7$\%$ of the 285 Ma old brachiopod carbonates (average $10.6 \pm 0.\%$, 1$\sigma$, $n=5$, (16)), which support the primary nature of our boron isotope data.

3.2 Environmental controls on the boron isotope composition

The speciation of boron in seawater is predominantly pH dependent with minor controls from temperature, salinity and pressure (50). In our model we consider a dynamic temperature effect on $pK_B$ to calculate the pH of the seawater from the boron isotope composition preserved in Permo-Triassic carbonate (see SM 4 and 5) however below we evaluate geological evidence to consider whether these variables could drive the trends seen in our data.
3.2.1 Temperature

Oxygen isotope data preserved in conodont apatite and low-Mg calcite brachiopods from Permian-Triassic sections in Iran document tropical sea surface temperatures (SST) of 27–33°C during the Changhsingian with a negative shift in $\delta^{18}O$ starting at the extinction horizon, translating into a warming of SSTs to well over 35°C in the mid-Griesbachian (51). The results are consistent with SSTs of the South Chinese sections, where a rapid increase in seawater temperature from about 25°C to 36°C across the Permian-Triassic section was proposed based on conodont apatite (6). Since the dissociation constant of boric acid ($pK_B$) decreases with increasing temperature (50), the proposed increase in SST could drive an increase in the B isotope composition of the carbonates precipitated at the time of global warming and imply an increase in ocean pH, even if ocean pH stayed stable. Using the $pK_B$ data from (50), the potential increase in SST at a given pH of 8 would drive an increase in $\delta^{11}B$ of the carbonates by 2‰ and generate an artificial increase of < 0.2 pH units. Consequently, it could be argued that our calculated pH variations are in essence the result of an increase in sea surface temperatures.

However, the oxygen isotope pattern (51) shows a continuous increase in temperatures across the Permian-Triassic boundary and a thermal maximum in the mid-Griesbachian (~251.85 Ma). Instead our data show a sharp increase in $\delta^{11}B$ and ocean pH in the Late Permian, well before the increase in temperatures at EP1. The slight variability in $\delta^{11}B$ above the PTB, however, could be driven by temperature variations.
3.2.2 Salinity

Similar to temperature, the pK_B is sensitive to salinity and increases with decreasing salinity \((52)\). To drive significant salinity-associated isotope variations across the Permo-Triassic boundary, drastic changes in salinity (e.g. down to 25 psu compared to 35 psu) would be necessary. However, even if modelled sea surface salinity values for the late Permian indicate generally more saline conditions than present day \((52)\), sea surface salinity values for e.g. Iran and South China still range between 34 and 35 psu \((51)\) and will not have a significant effect on our pH calculation. These samples come from an exclusively shallow water environment far from any freshwater input, and so decreases in salinity would not affect our pH interpretations. The depositional environment here ranges between open water ooid shoals to open and restricted lagoon settings, which results in cyclic deposition on the scale of 5m. A shift toward more restricted settings could drive increases in salinity that would affect the \(\delta^{11}B\) record; however, these depositional cycles are not on the same scale as the secular trends seen in \(\delta^{11}B\).

3.2.3 Water Depth

Permo-Triassic seawater pH values have been reconstructed assuming carbonate precipitation at sea surface conditions. Modern bathymetric pH and temperature profiles from the tropics show that pH can decrease by up to \(-0.2\) units and temperature can drop by \(15^\circ\)C in the first 300 m \((53)\). Thus the B isotope composition of carbonates precipitated at greater water depths would be more negative compared to surface precipitates. This potential depth effect is thought to be of minimal influence to the Wadi Bih carbonates due to the exclusively shallow marine (subtidal to intertidal) nature of the succession.
Consequently, uncertainties in the $\delta^{11}$B-ocean pH relationship potentially introduced by changes in temperature, salinity, bathymetry or biofacies would not be able to produce the observed B isotope pattern with the sharp increase in the mid-Changhsingian (~252.04 Ma) and the temporary decrease in the mid-Griesbachian (~251.88 Ma), but would be capable of explaining some of the slight variations across the PTB.

4. Boron-pH calculations

The boron isotope composition of marine carbonates is used to reconstruct seawater pH values and atmospheric pCO$_2$ concentrations (e.g. 54-58). The application of the B isotope system as a proxy for ocean pH is based on the observation that the fractionation factor for isotope exchange between the two different speciation of boron (B(OH)$_3$ and B(OH)$_4^-$) is pH sensitive and produces significant and traceable changes in the isotopic composition of carbonates (e.g. 57).

The carbonate-associated boron isotopic composition $\delta^{11}$B$_{\text{carb}}$ is assumed to be equal to that of seawater B(OH)$_4^-$. The isotopic composition of the two boron species B(OH)$_4^-$ and B(OH)$_3$ is determined by the isotopic fractionation factor $\alpha_{B3:B4} = 1.0272$ (59), the speciation (a strong function of pH, with smaller dependencies on temperature, pressure and salinity), and the overall isotopic composition of seawater $\delta^{11}$B$_{\text{sw}}$. The relationship between pH and $\delta^{11}$B$_{\text{carb}}$ is given by:

$$\text{pH} = pK_B - \log \left[ \frac{\delta^{11}B_{\text{sw}} - \delta^{11}B_{\text{carb}}}{\delta^{11}B_{\text{sw}} - \alpha_{B3:B4} \cdot \delta^{11}B_{\text{carb}} - 1000 \cdot (\alpha_{B3:B4} - 1)} \right]$$

where the effective dissociation constant $pK_B$ includes the temperature, pressure and salinity dependence. We dynamically calculate $pK_B$ using CO2SYS-MATLAB v1.1 (60) (detailed in SM 5), which is consistent with the calculation and constants used by (61).
A prerequisite for reconstruction of past ocean pH values via B isotope data is the
knowledge of the primary B isotope composition $\delta^{11}B_{SW}$ of the ambient seawater. The B isotope
composition of modern seawater is regarded as being homogeneous with a $\delta^{11}B$ value of 39.5‰
(54). However, recent work on Precambrian to Phanerozoic carbonates and evaporites has shown
that the B isotope composition of seawater was highly variable in the geological past (16, 45, 46)
driven mainly by variations in the global boron budget during Earth history (23), exceeding the
residence time of B in seawater. Permo-Triassic seawater have been calculated based on changes
in processes controlling the oceanic boron budget, e.g. oceanic crust production rate and
continental boron flux (16) and suggests $\delta^{11}B_{SW}$ values of ~38‰ for the early Permian (285 Ma,
Late Sakmarian) and ~34‰ just before the PTB (16).

Given this uncertainty in $\delta^{11}B_{SW}$, we consider a range of values, determined by the
overall consistency of the $\delta^{11}B_{carb}$ data with model-derived constraints on the seawater carbonate
chemistry and hence pH, resulting in an envelope for the pH calculation. The model scenarios
encompass the range of previous estimates for background Early Permian conditions (13), which
suggest either high $pCO_2$ with lower pH ($CO_2Hi$: ~10 PAL, pH ~7.5), or low $pCO_2$ with higher
pH ($CO_2Lo$: ~3 PAL, pH ~8). In our model we consider these two scenarios with corresponding
seawater boron isotopic composition ($\delta^{11}B_{SW} = 34‰$ and 36.8‰) required to reproduce the
observed $\delta^{11}B_{carb}$ (see SM Section 6 for further details of the model scenarios).

We illustrate the effect of uncertainties in $\delta^{11}B_{SW}$ and temperature on pH, and the overall
consistency with the $\delta^{11}B_{carb}$ data in Figure S3 and Table S1 (note that the full model described
in SM 4 also includes a dynamic calculation of temperature). The lowest $\delta^{11}B_{SW} =34‰$ and
highest pH considered (scenario $CO_2Lo$) is effectively constrained by the model limitation on the
highest pH values immediately prior to EP1. The highest $\delta^{11}B_{SW} =36.8‰$ and lowest pH
(scenario CO$_2$Hi) is effectively constrained by the limit of propagated uncertainty (2σf) on the
lowest observed $\delta^{11}$B$_{\text{carb}}$ combined with the non-linearity of the B isotope system.

An additional uncertainty in interpreting $\delta^{11}$B$_{\text{carb}}$ is introduced by any potential offset or
fractionation between seawater borate $\delta^{11}$B(OH)$_4^-$ and $\delta^{11}$B$_{\text{carb}}$. As shown by (59), the laboratory
measured fractionation of abiotic carbonate (61) shows both an offset relative to that of the
artificial seawater, and a shallower slope with increasing pH. As we consider $\delta^{11}$B$_{\text{SW}}$ as a model
parameter to be determined, an overall offset is effectively subsumed within this. However a
shallower slope than that used here ($^{11-10}$K$_B$ = 1.0272 [ref 59], cf the one given for inorganic
carbonates (1.0267; [ref 62])) would require a larger pH change for a given observed change in
$\delta^{11}$B$_{\text{carb}}$. Sanyal et al. (63) published B isotope values for inorganic calcite precipitates at three
different pH conditions - 7.9, 8.3, and 8.6. This same experimental inorganic calcite data and
associated estimates of $^{11-10}$K$_B$ in seawater were also presented by Klochko et al. (59, 64). To
date, there is no agreement as to the actual deviation of Sanyal’s data (63) from the now
generally-accepted empirical fractionation factor given by Klochko et al (59). A best fit value of
1.0267 for the inorganic calcite precipitation was given by Pagani et al. (62). But by contrast, the
deviation between the inorganic carbonate values and the empirical fractionation appears much
bigger in Klochko et al. (59) and the best-fit value is given as 1.0260. This increased deviation is
explained by the difference in pH scale between natural or artificial seawater used for the
calibration experiments, and the experimental seawater pH measured on the (freshwater) NBS
scale. Klochko et al. (64) tries to address the deviations in $\delta^{11}$B of inorganic precipitates from
empirical calibration studies and concludes that boric acid incorporation may contribute to the
$^{11}$B enrichment observed in inorganic precipitates, especially at lower pH. They point out,
however, that all carbonates precipitated under controlled pH conditions were enriched in $^{11}\text{B}$ relative to seawater borate (63).

If we use the best fit value (1.0267) given by Pagani et al. (62) for the inorganic carbonates (Sanyal et al 2000) instead of the empirical value of Klochko et al. (59), then the offset for the majority of the data would be around 0.05 pH units. Visible changes to more acidic values would only appear at the lowermost pH estimates, but would still be less than 0.2 pH units and fall within the general uncertainty. If we take the 1.026 value, the offset would generally increase between ≤0.1 and 0.2 (pH range between ~8.4 and 7.8) but would indeed result in significantly lower pH values of up to 0.5 units for the acidification event.

Given the limited amount of experimental inorganic calcite data and this disagreement between the best-fit values, we have taken the simplest approach for the model representation and chosen to use the most generally-accepted empirical fraction factor given by Klochko et al. (59).
Figure S3 Effect of background $\delta^{11}\text{B}_{\text{SW}}$ and temperature on relationship between $\delta^{11}\text{B}_{\text{carb}}$ and pH (total scale), for conditions appropriate to low-latitude surface ocean (atmospheric pressure, salinity 35 psu, temperature 25°C (solid lines) and 35°C (dashed lines)). Three values are shown for $\delta^{11}\text{B}_{\text{SW}}$: 39.61‰ (the contemporary value) and two values consistent with the end Permian data. Data points and 2σ errors are overlaid for the $\delta^{11}\text{B}_{\text{SW}}$ 34‰ case.
5. Model Description

5.1 Overview

The overall model structure (shown in Figure S4) is essentially a superset of carbon cycle models previously applied to the end Permian (65, 66, 67), with additional consideration of the marine sulphur cycle. The model includes a three box ocean model as the minimum needed to demonstrate the effect of the biological pump on vertical DIC gradients and ocean redox state. The model is implemented as a set of coupled differential equations for the time evolution of reservoirs (Table S3), exchanging fluxes according to air-sea exchange, ocean circulation, applied external forcings and perturbations, and the biogeochemical processes described in Table S5. Model constants are defined in Table S4. The model implements an open inorganic carbon cycle, with atmospheric $p$CO$_2$ and marine DIC and Alk determined by the feedbacks between land-surface carbonate and silicate weathering and marine carbonate deposition. Oxidative weathering, volcanic degassing, and land and marine organic carbon burial are specified as forcings, as is marine phosphorus and hence productivity.
Table S3 Model reservoirs

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Initial size</th>
<th>Description</th>
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</thead>
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<tr>
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<tr>
<td>CO₂</td>
<td>eqb&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Atmospheric CO₂</td>
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<tr>
<td><strong>Ocean</strong></td>
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<td></td>
</tr>
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<td>DIC&lt;sub&gt;(s,h,d)&lt;/sub&gt;</td>
<td>eqb&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Total carbon</td>
</tr>
<tr>
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</tr>
<tr>
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<td>eqb&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Oxygen</td>
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<td>Phosphate</td>
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<tr>
<td>Ca</td>
<td>10.28 mM / kg-sw</td>
<td>Calcium (single reservoir)</td>
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</table>

Figure S4 Model schematic. Ocean is represented by three boxes (s, h, d), with well-mixed atmosphere box a. Biogeochemical fluxes are shown in green, ocean circulation in blue. Biogeochemical reservoirs are shown as ovals.
*set by initial spin-up to steady-state.*

### Table S4 Model fluxes, constants, and forcings.

<table>
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<tr>
<th>Flux</th>
<th>Model Parameter</th>
<th>Value</th>
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<th>Description</th>
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<td>Redfield N:P ratio</td>
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</tr>
<tr>
<td>( f_{mocb} )</td>
<td>( k_{carbsedshallow} )</td>
<td>varies(^a)</td>
<td>mol CaCO(_3) yr(^{-1})</td>
<td>Marine carbonate burial</td>
</tr>
<tr>
<td>( f_{mocb} )</td>
<td>( k_{2,mocb} )</td>
<td>5x10(^{12})</td>
<td>mol C yr(^{-1})</td>
<td>Marine organic carbon burial</td>
</tr>
</tbody>
</table>

\(^a\)parameters \( k_{silw}, k_{12,ccdeg}, k_{carbsedshallow} \) are per-scenario external forcings.
### Table S5: Biogeochemical processes

<table>
<thead>
<tr>
<th>Flux</th>
<th>Biogeochemical transformation</th>
<th>Stoichiometry</th>
<th>Rate</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO$_2$(a)</td>
<td>DIC</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>land surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{\text{carbw}}$</td>
<td>CO$_2$ + H$_2$O + CaCO$_3$</td>
<td>-1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ Ca$^{2+}$ + 2HCO$_3^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{\text{silw}}$</td>
<td>2CO$_2$ + H$_2$O + CaSiO$_3$</td>
<td>-2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ SiO$_2$ + Ca$^{2+}$ + 2HCO$_3^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{\text{oxidw}}$</td>
<td>CH$_2$O + O$_2$ $\rightarrow$ CO$_2$ + H$_2$O</td>
<td>1</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$f_{\text{locb}}$</td>
<td>CO$_2$ + H$_2$O $\rightarrow$ CH$_2$O + O$_2$</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>marine</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{\text{exp}}$</td>
<td>CO$_2$ + H$_2$O + xP $\rightarrow$ CH$_2$OP$_x$ + O$_2$</td>
<td>-1</td>
<td>0</td>
<td>1+</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$OP$_x$ + O$_2$ $\rightarrow$ CO$_2$ + H$_2$O + xP</td>
<td>1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$OP$_x$ + $\frac{1}{2}$SO$_4^{2-}$ $\rightarrow$ HCO$_3^-$ + xP + $\frac{1}{2}$H$_2$S</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$S + 2O$_2$ $\rightarrow$ SO$_4^{2-}$ + 2H$^+$</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>$f_{\text{mocb}}$</td>
<td>Ca$^{2+}$ + HCO$_3^-$ $\rightarrow$ H$^+$ + CaCO$_3$</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H$_2$S + Fe(OH)$_3$ $\rightarrow$ FeS$_2$ + $\frac{1}{2}$H$_2$ + 3H$_2$O</td>
<td>0</td>
<td>0</td>
<td>-0.5</td>
</tr>
<tr>
<td>$f_{\text{mocb}}$</td>
<td>CO$_2$ + H$_2$O $\rightarrow$ CH$_2$O + O$_2$</td>
<td>-1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

* a contribution from nitrate, assumed at Redfield ratio.
5.2 Detailed description

5.2.1 pCO$_2$ and temperature

Global mean temperature $T_{\text{mean}}$ is calculated from atmospheric pCO$_2$ using the energy balance model as in COPSE (68, 69), with solar insolation appropriate for 250 Mya. Marine temperature $T_{O(s,h,d)}$ is calculated from the global mean assuming a fixed high-low latitude temperature difference and minimum temperature of 2.5°C, with $T_{O(s)}=T_{\text{mean}}+6.5$ °C and $T_{O(h,d)}=\max(T_{\text{mean}}-12.5,2.5)$ °C.

5.2.2 Land surface weathering, degassing, and organic carbon burial

Land surface weathering is essentially a stripped-down version of that in COPSE (69), with carbonate and silicate weathering included but sulphur weathering and the long-timescale sedimentary reservoirs for sulphur and carbon are omitted. Atmospheric oxygen is fixed at the present-day value. Silicate and carbonate weathering are controlled by atmospheric pCO$_2$ and temperature with functional forms:

$$f_{\text{silw}} = k_{\text{silw}} e^{0.090(T_{\text{mean}}-T_0)[1 + 0.038(T_{\text{mean}} - T_0)]^{0.65}} \left( \frac{2 \text{ pCO}_2}{1 + \text{pCO}_2} \right)$$  \hspace{1cm} (S1)

$$f_{\text{carbw}} = k_{\text{carbw}} \left[ 1 + 0.087(T_{\text{mean}} - T_0) \right] \left( \frac{2 \text{ pCO}_2}{1 + \text{pCO}_2} \right)$$  \hspace{1cm} (S2)

where $T_0=15$ °C.

Atmospheric CO$_2$ is consumed, and carbon, alkalinity and calcium supplied to the ocean, according to the stoichiometry defined in Table S5. Volcanic degassing, oxidative weathering, and land organic carbon burial are prescribed as forcings.
5.2.3 Marine circulation and air-sea exchange

Marine circulation is defined by a thermohaline circulation $T$, and high-latitude – deep exchange $f_{\text{hd}}$. The marine box model includes $P$, $O$, DIC, Alk, SO$_4$, H$_2$S as per-box prognostic variables, along with DIC $\delta^{13}$C. Marine carbonate chemistry is calculated using a modified version of CO2SYS-MATLAB v1.1 (60), extended to include sulphide alkalinity using the constants tabulated by (70). Air-sea exchange of oxygen and CO$_2$ assume a fixed piston velocity and temperature-dependent solubility.

5.2.4 Marine productivity and burial

Productivity and hence the biological pump are controlled by the marine phosphorus circulation. Biomass is produced in the surface ocean boxes, and exported and remineralized in the deep box according to the processes and stoichiometries defined in Table S5. Productivity in the ‘s’ box is specified to consume all phosphorus down to negligible concentration. Productivity in the ‘h’ box is specified to consume a fraction 0.18 of input phosphorus. Remineralization in the deep ocean box consumes oxygen down to a limiting concentration of 1$\mu$M and thereafter reduces sulphate to sulphide.

Shallow-water carbonate deposition occurs in the ‘s’ box only and is controlled by aragonite saturation state and a parameter representing a combination of shelf area and calcification effectiveness, ie a ‘Neritic’ ocean without pelagic calcifiers (71), functional form $k_{\text{carbsedshallow}}*(\Omega_{\text{aragonite}} - 1)^{1.7}$. Ocean carbonate compensation is not included, on the basis this will be small for a ‘Neritan’ ocean.

Marine organic carbon burial from the ‘s’ box and pyrite burial from the ‘d’ box are imposed as forcings. Given the uncertainties in controls on phosphorus input over the end-Permian interval, the marine phosphorus cycle is semi-closed (i.e. weathering feedback on phosphorus input is not included), with imposed perturbations (forcings) to source/sink
balance (riverine input vs burial) applied as inputs to the ‘s’ box to control phosphorus concentration.

5.2.5 Carbon isotopes

Carbon isotopes are implemented with additional reservoirs for each of atmospheric CO$_2$ and marine DIC$_{(s,h,d)}$. Air-sea exchange fractionates according to the temperature-dependent equilibrium and kinetic factors determined by Zhang et al. (72). Marine export production is at fixed fractionation relative to DIC, with $\delta^{13}C_{\text{exp(s,h)}} = \delta^{13}\text{DIC}_{(s,h)} - 25 \text{‰}$.

Volcanic degassing, carbonate weathering, and oxidative weathering are assumed to add carbon at fixed fractionations of -4.9‰, 2.65‰, and -25‰ respectively. Atmospheric CO$_2$ consumed by silicate and carbonate weathering (and added to the ocean ‘s’ box as DIC) is fractionated relative to atmospheric CO$_2$ according to the freshwater fractionation of Zhang et al. (72).

Land and marine organic carbon burial is at fixed fractionation relative to atmospheric CO$_2$ and marine DIC, with $\delta^{13}C_{\text{locb}} = \delta^{13}\text{CO}_2 - 19 \text{‰}$ and $\delta^{13}C_{\text{mocb}} = \delta^{13}\text{DIC}_{(s)} - 25 \text{‰}$. Marine inorganic carbon burial is assumed to not fractionate relative to DIC$_{(s)}$.

5.2.6 Boron isotopes

Carbonate-associated boron isotopic composition $\delta^{11}\text{B}_{\text{carb}}$ is assumed to be equal to that of seawater B(OH)$_4^-$ . Speciation of B(OH)$_4^-$ and B(OH)$_3$ is calculated using CO2SYS-MATLAB v1.1 (60). Isotopic composition is then calculated from speciation $x_{\text{bO}_4} = [\text{B(OH)}_4^-]/[\text{B total}]$ and seawater $\delta^{11}\text{B}_{\text{SW}}$ as

$$\delta^{11}\text{B}_{\text{carb}} = \frac{\delta^{11}\text{B}_{\text{sw}} - 1000(1 - x_{\text{bO}_4})(\alpha_B - 1)}{\alpha_B - x_{\text{bO}_4}(\alpha_B - 1)}$$

with the isotopic fractionation factor $\alpha_B = 1.0272$. 


5.2.7 Model spinup and steady state

The model pCO$_2$ steady-state is defined by the imposed degassing rate, organic carbon burial and oxidation, and silicate weathering parameterisations, where these together define a unique value for the steady-state atmospheric pCO2 and temperature where $f_{\text{deg}} + f_{\text{oxid}} = f_{\text{sil}} + f_{\text{loc}} + f_{\text{moc}}$. During spin-up, the ocean chemistry and hence atmosphere-ocean CO$_2$ partitioning adjust (on the silicate weathering timescale of ~100kyr) to a steady-state, with the aragonite saturation state adjusting such that carbonate burial balances inputs from carbonate and silicate weathering.

5.2.8 Sensitivity to seawater composition

The Mg and Ca composition of end-Permian seawater (as determined from fluid inclusions) is consistent with that of modern seawater ([Mg] = 53 mmol/kg, [Ca] = 10.3 mmol/kg), but with large uncertainties (6). Sulphate concentration may have been much lower than modern values (73, 74). We estimate the uncertainties in carbonate system chemistry following the approach of (75). We estimate the effect on $K_1$ and $K_2$ from model results (74) as:

$$
\frac{K_1^*}{K_1} = 1 + 0.155 \frac{\Delta [Mg^{2+}]}{[Mg^{2+}]_m} + 0.033 \frac{\Delta [Ca^{2+}]}{[Ca^{2+}]_m} - 0.019 \frac{\Delta [SO_4^{2-}]}{[SO_4^{2-}]_m}
$$

$$
\frac{K_2^*}{K_2} = 1 + 0.641 \frac{\Delta [Mg^{2+}]}{[Mg^{2+}]_m} + 0.071 \frac{\Delta [Ca^{2+}]}{[Ca^{2+}]_m} - 0.054 \frac{\Delta [SO_4^{2-}]}{[SO_4^{2-}]_m}
$$

where subscript $m$ refers to modern values and an asterix to end-Permian values. Taking extremal values $[Mg^{2+}]*/[Mg]_m=0.5$, $[Ca^{2+}]*/[Ca]_m=2$, $[SO_4^{2-}]*/[SO_4^{2-}]_m=0.1$, we have $K_1^*/K_1=1-0.078+0.033+0.0171=0.972$ or $pK_1^*=pK_1+0.012$ (or for $[Mg^{2+}]$ alone, $K_1^*/K_1=0.92$, $pK_1^*=pK_1+0.035$). For a fixed pCO$_2$, this implies a corresponding decrease in $[HCO_3^-]$ and hence DIC inventory, or equivalently an increase in pH for the same DIC content. The corresponding effect on $K_2$ is much larger, $K_2^*/K_2=1-$
We estimate the effect of Mg concentration on the calcite solubility constant $K_{sp}$ using the parameterisation given by (76) as:

$$\frac{K_{sp}^*}{K_{sp,m}} = 1 - 0.0833 \left( \frac{[\text{Mg}^{2+}]_m}{[\text{Ca}^{2+}]_m} \cdot \frac{[\text{Mg}^{2+}]^*}{[\text{Ca}^{2+}]} \right)$$

which gives $K_{sp}^*/K_{sp}=1-0.33$.

This sensitivity study shows that the uncertainty in $K_1$ therefore introduces only a small uncertainty in pH ($\sim 0.03$) or equivalently a $\sim 10\%$ uncertainty in DIC inventory relative to pCO$_2$. The combined uncertainties in $K_2$, $K_{sp}$ and $[\text{Ca}^{2+}]$ are larger, introducing corresponding uncertainties in calcite saturation state. However, within the model employed here, this is effectively absorbed into a rescaling of the parameter $k_{\text{carbsedshallow}}$.

### 6- Model Scenarios

Given the uncertainty in the absolute value of the seawater boron isotope composition (section S4), we consider two scenarios with initial steady-state conditions as in Table S6: scenario CO$_2$Hi uses $\delta^{11}$B$_{SW}=36.86$, and CO$_2$Lo uses $\delta^{11}$B$_{SW}=34$. Here ocean pH depends on the combination of atmospheric pCO$_2$ and carbonate saturation state. Atmospheric pCO$_2$ (set by the ratio of net carbon sources : silicate weatherability) is tuned to 3 or 10 PAL, encompassing the range of conditions considered by previous model studies (77, 78, 79). Ocean carbonate saturation state is set by carbonate sedimentation efficiency parameter $k_{\text{carbsedshallow}}$, which represents a combination of shelf area x deposition rate. A summary of scenarios required to explain the three events in our $\delta^{11}$B data are given in Table S7 and explored in further detail below.
### Table S6 Steady-state initial conditions summary

<table>
<thead>
<tr>
<th><strong>Parameters</strong></th>
<th><strong>CO₂Hi</strong></th>
<th><strong>CO₂Lo</strong></th>
<th><strong>Units</strong></th>
<th><strong>Description</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{12\text{,ccdeg}}$</td>
<td>$1.18x10^{12}$</td>
<td>$1.18x10^{12}$</td>
<td>mol CO₂ yr⁻¹</td>
<td>Degassing</td>
</tr>
<tr>
<td>$k_{17\text{,oxidw}}$</td>
<td>$5x10^{12}$</td>
<td>$5.92x10^{12}$</td>
<td>mol C yr⁻¹</td>
<td>Oxidative weathering</td>
</tr>
<tr>
<td>$k_{\text{silw}}$</td>
<td>$2.40x10^{12}$</td>
<td>$6.60x10^{12}$</td>
<td>mol CaSiO₃ yr⁻¹</td>
<td>Silicate weatherability</td>
</tr>
<tr>
<td>$k_{\text{carbsedshallow}}$</td>
<td>$18.43x10^{12}$</td>
<td>$1.44x10^{12}$</td>
<td>mol CaCO₃ yr⁻¹</td>
<td>Marine carbonate burial efficiency</td>
</tr>
</tbody>
</table>

### Steady-state conditions

<table>
<thead>
<tr>
<th><strong>Parameter</strong></th>
<th><strong>Condition</strong></th>
<th><strong>Value</strong></th>
<th><strong>Unit</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>pCO₂, ppm</td>
<td></td>
<td>2800</td>
<td>845</td>
</tr>
<tr>
<td>$T_{\text{mean}}$</td>
<td></td>
<td>22.18</td>
<td>14.94°C</td>
</tr>
<tr>
<td>$T_{\text{O(s)}}$</td>
<td></td>
<td>28.7</td>
<td>21.44°C</td>
</tr>
<tr>
<td>$\Omega_{\text{arag(s)}}$</td>
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<td>2.44</td>
<td>6.15</td>
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<tr>
<td>pH</td>
<td></td>
<td>7.51, 7.46, 7.0</td>
<td>8.02, 7.99, 7.60</td>
</tr>
<tr>
<td>DIC total</td>
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<td>$5.53x10^{18}$</td>
<td>$6.01x10^{18}$</td>
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<tr>
<td>$\delta^{13}\text{DIC}_{(s)}$</td>
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<td>$+3.32$</td>
<td>$+2.97$‰</td>
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</table>

### Fluxes

<table>
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<th><strong>Condition</strong></th>
<th><strong>Value</strong></th>
<th><strong>Unit</strong></th>
<th><strong>Description</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{\text{carbw}}$</td>
<td></td>
<td>$27.46x10^{12}$</td>
<td>$15.58x10^{12}$</td>
<td>mol CaCO₃ yr⁻¹</td>
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<tr>
<td>$f_{\text{silw}}$</td>
<td></td>
<td>$6.80x10^{12}$</td>
<td>$7.72x10^{12}$</td>
<td>mol “CaSiO₃” yr⁻¹</td>
</tr>
<tr>
<td>$f_{\text{ccdeg}}$</td>
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<td>$11.80x10^{12}$</td>
<td>$11.80x10^{12}$</td>
<td>mol CO₂ yr⁻¹</td>
</tr>
<tr>
<td>$f_{\text{mccb}}$</td>
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<td>$34.26x10^{12}$</td>
<td>$23.30x10^{12}$</td>
<td>mol CaCO₃ yr⁻¹</td>
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<tr>
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<td>Time</td>
<td>Scenario</td>
<td></td>
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</tr>
<tr>
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<td>-----------</td>
<td>----------------------------------------------------------------</td>
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</tr>
<tr>
<td></td>
<td></td>
<td><strong>Scenario</strong></td>
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</tr>
<tr>
<td></td>
<td></td>
<td><strong>CO₂Hi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ¹¹B&lt;sub&gt;sw&lt;/sub&gt;=36.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>CO₂Lo</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ¹¹B&lt;sub&gt;sw&lt;/sub&gt;=34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH rise</td>
<td>252.25 Ma</td>
<td>Marine productivity increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>252.05 Ma</td>
<td>Carbonate sedimentation efficiency decrease</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pyrite deposition, Carbonate weathering increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ¹³C drop, stable pH</td>
<td>252.00 Ma</td>
<td>Land organic carbon burial decrease</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>251.95 Ma</td>
<td>Slow (~50kyr) isotopically light carbon addition.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidification, δ¹³C change</td>
<td>no</td>
<td>251.88 Ma Rapid (10kyr) isotopically heavy carbon addition</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 6.1 Mechanisms for pH rise

The rise in δ¹¹B at 252.05 Ma corresponds to a rise in pH from 7.5 to 8.0 for scenario CO₂Hi, and from 8.0 to 8.3 for scenario CO₂Lo. Given the major upheavals in the Earth system at the end-Permian, multiple mechanisms including changes in silicate and carbonate weathering, and marine changes in calcification and due to anoxia may potentially contribute to pH rise, and we use model sensitivity studies to determine potential constraints. We first review evidence for each mechanism, then summarize the model sensitivity studies and propose plausible scenarios involving multiple drivers.
6.1.1 Carbonate weathering

The overall high weathering rates across the Permian-Triassic boundary also imply an increase in carbonate weathering, possibly combined with any direct effect from chemical weathering of eroded clastic material itself.

There is also direct evidence for later sea-level regression and subaerial weathering of the shallowest sections of the S. China carbonate platform, coincident with EP1 (20) which may contribute to maintaining pH over this interval. To estimate an order of magnitude for enhanced carbonate shelf weathering: $10^{18}$ mol CaCO$_3$, density 2.8 g cm$^{-3}$ has volume 36,000 km$^3$, or 100m x $3.6x10^5$km$^2$, or 1800km of 200km wide shelf; this would provide a weathering flux of $10^{13}$ mol CaCO$_3$ yr$^{-1}$ for 100 kyr, comparable to the background carbonate weathering rate.

6.1.2 Decrease in calcification effectiveness

Overall global biotic calcification effectiveness is determined by the combination of available shelf area, and local ecosystem-dependent rates. A reduction in area of deposition could be because anoxic/euxinic waters extend onto the shelf bottom precluding those parts from hosting deposition, and/or because there is a sea level change reducing shelf area. The input of clastics prior to EP1 could also reduce carbonate production as a result of ecosystem impacts (80, 81).

6.1.3 Productivity-driven ocean anoxia, sulphate reduction, and pyrite burial

Multiple lines of evidence suggest a (large) expansion of oxygen minimum zones prior to the PT boundary, while the deep ocean remains suboxic. These include U isotope evidence for ~6x increase in anoxic fraction (82), extensive pyrite deposition (83), and GCM studies (84) illustrating the spatial distribution of anoxia.
We represent productivity-driven ocean anoxia by increasing marine phosphorus from the present-day value to 2.3x present (the value used by (66). This is achieved by adding phosphorus to the marine ‘s’ reservoir (representing a net excess of riverine input over sediment output) at rate $3.9 \times 10^{10}$ mol yr$^{-1}$ over the interval 252.15 – 252.05 Ma (cf present-day riverine input $\approx 2 \times 10^{10}$ mol yr$^{-1}$) (64). This results in pCO$_2$ drawdown as a result of the increased biological pump, and in sulphate reduction leading to $\sim 50 \, \mu$M H$_2$S in the ‘d’ box. Note that sulphate reduction increases alkalinity / pH in the ‘d’ box by $\Delta$pH $\sim 0.1$, but as the S redox shuttle is completed by sulphide oxidation at the base of the oxic surface box, this has no effect on the pH of the oxic surface ocean.

High rates of pyrite formation are seen at and before EP1 (83, 85). Pyrite burial results in a net alkalinity source (86). We assume that pyrite deposition is a water-column process, hence is limited by the availability of iron and sulphide. The most limiting factor for the scenarios considered here is iron. To quantify this, we estimate pyrite deposition rate sustainable over a timescale of $\sim$100kyr as $\sim 1.25 \times 10^{12}$ mol FeS$_2$ yr$^{-1}$, based on availability of reactive iron Fe$_{HR}$ (in the contemporary oxic ocean, Fe$_{HR}$ total input to the ocean is $\sim 6.8 \times 10^{12}$ mol yr$^{-1}$, of which only $\sim 1.3 \times 10^{12}$ mol yr$^{-1}$ gets to the deep ocean (87). Sulphide availability is determined by anaerobic organic carbon remineralisation in the ‘d’ box, which is a model-determined fraction of total export production $\sim 10^{14}$ mol yr$^{-1}$, and is less limiting than iron for the scenarios considered here. This assumes that sulphate for remineralisation (and hence sulphide availability) is unconstrained by marine sulphur availability, ie that the marine sulphate reservoir is drawn down. This is supported by (or at least consistent with) the data indicating low early Triassic marine sulphate, $< 4$mM (75, 88).
6.1.4 Silicate weathering

Anomalously high sediment fluxes across the Permian-Triassic boundary (80, 81) imply soil loss and increased exposure of highly weatherable rock surfaces, with increases in both physical and chemical weathering. Early Siberian traps emplacement and an increase in area of weatherable basalt also may contribute to an increase in overall silicate weatherability. The main increase in silicate weathering is seen in the Griesbachian but increases may have accompanied the carbon injection for EP1.

6.1.5 Combined scenarios

We summarize the effect of illustrative perturbations for the separate contribution of each potential driver of pH increase in Table S8. Perturbations were applied to the CO$_2$Lo steady state at 251.95Ma (corresponding to the pH rise seen in the $\delta^{11}$B data), with effect shown 100kyr later (at EP1). The marine carbonate system responds on a timescale of ~10kyr, hence reaches a steady state source-sink balance, however the timescale for land-surface weathering feedbacks is >~100 kyr hence the system does not reach a steady state. The dynamic response is included in the full scenarios.

As shown in figure S5, the perturbations fall into two groups. Increases in silicate weatherability and pyrite deposition leave carbonate input rate and calcification output essentially unchanged, hence result in changes to atmospheric pCO$_2$ at nearly constant saturation state. Changes to atmospheric pCO$_2$ alone are unable to produce a change in pH or $\delta^{11}$B as large as that seen in the data without implausibly low pCO$_2$ and hence temperature, hence these cannot be the sole drivers of pH increase. Reductions in calcification effectiveness or increases in carbonate inputs change both the carbonate system saturation state and atmospheric pCO$_2$, resulting in a much larger increase in pH for a given decrease in pCO$_2$. A major contribution from either or both of these mechanisms is therefore required.
The results from the perturbations study demonstrate that all mechanisms may contribute to pH rise, with a major contribution from either or both carbonate input and decrease in calcification effectiveness required. Given the most likely case where multiple mechanisms all contribute, we construct scenarios with a decrease in calcification effectiveness as the major component and smaller contributions from pyrite burial and carbonate weathering (Figure S6). The perturbations considered for the two scenarios are summarized in Table S9 and the dynamic response is shown in Figure S6.
Figure S5 Effect of illustrative perturbations (defined in Table S8) on carbonate system properties for atmosphere and ocean surface (s) box. Contours show carbonate system parameters for a constant temperature of 25 °C, salinity 35 psu, pressure 1 atm, hence do not exactly correspond to the full model results with varying temperature.
Figure S6 Scenario CO$_2$Lo: Contributions to pH increase. ‘SA’: effect of calcification effectiveness decrease. ‘+prod’ effect of increased marine productivity and anoxia. ‘+pyr’ pyrite burial, and ‘+carb’ carbonate weathering.
Table S8 Sensitivity study for pH rise mechanisms. Perturbations applied to steady-state CO$_2$Lo at 252.05Ma, effect shown at 251.95Ma.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Perturbation</th>
<th>pH$_{tot(s)}$</th>
<th>$\delta^{13}$B$_{(s)}$</th>
<th>$\Omega_{arag(s)}$</th>
<th>pCO$_2$</th>
<th>T$_{mean}$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>steady-state</td>
<td>none</td>
<td>8.02</td>
<td>11.83</td>
<td>6.15</td>
<td>845</td>
<td>14.94</td>
<td>Error! Reference source not found.</td>
</tr>
<tr>
<td>CO$_2$Lo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>'calc eff decrease'</td>
<td>$k_{carbosedshallow}$ 14.4x10$^{11}$</td>
<td>$\rightarrow$  +0.266  +2.72  +5.55</td>
<td></td>
<td>-351</td>
<td>-2.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.47x10^{11}$ (ie x 0.17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pyr deposition</td>
<td>$k_{carbosedshallow}$ 14.4x10$^{11}$</td>
<td>$\rightarrow$  +0.36  +3.78  +8.2</td>
<td></td>
<td>-446</td>
<td>-3.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.23x10$^{11}$ (ie x 0.085)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>'x1': 1.25x10$^{12}$ mol FeS$_2$ yr$^{-1}$</td>
<td>+0.083  +0.71  -0.03</td>
<td></td>
<td>-213</td>
<td>-1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>'x2': 2.5x10$^{12}$ mol FeS$_2$ yr$^{-1}$</td>
<td>+0.155  +1.36  +0.12</td>
<td></td>
<td>-347</td>
<td>-2.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>'x4': 5x10$^{12}$ mol FeS$_2$ yr$^{-1}$</td>
<td>+0.318  +3.062  +0.46</td>
<td></td>
<td>-557</td>
<td>-4.66</td>
<td>~ upper limit from Fe availability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>carb input</td>
<td>$+1x$: add 15x10$^{12}$ mol CaCO$_3$ yr$^{-1}$</td>
<td>+0.082  +0.77  +1.44</td>
<td></td>
<td>-130</td>
<td>-0.81</td>
<td>+1x = approx 2x background weathering rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ocean carb deposition rapidly compensates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+2x = ~3x background weath rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+3x = ~4x background weath rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+2x$: add 30x10$^{12}$ mol CaCO$_3$ yr$^{-1}$</td>
<td>+0.147  +1.41  +2.76</td>
<td></td>
<td>-219</td>
<td>-1.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+3x$: add 45x10$^{12}$ mol CaCO$_3$ yr$^{-1}$</td>
<td>+0.20  +1.97  +3.99</td>
<td></td>
<td>-285</td>
<td>-1.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>silw weath increase</td>
<td>$x2$ $k_{silw}$ 6.60x10$^{12}$ $\rightarrow$ 13.2x10$^{12}$</td>
<td>+0.14  +1.19  +0.35</td>
<td></td>
<td>-329</td>
<td>-2.30</td>
<td>‘Weatherability’: drives pH primarily via pCO$_2$ decrease</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$x4$ $k_{silw}$ 6.60x10$^{12}$ $\rightarrow$ 26.4x10$^{12}$</td>
<td>+0.32  +3.08  +0.57</td>
<td></td>
<td>-588</td>
<td>-5.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>calc eff + pyr</td>
<td>$k_{carbosedshallow}$ 14.4x10$^{11}$</td>
<td>$\rightarrow$  +0.37  +3.91  +5.78</td>
<td></td>
<td>-501</td>
<td>-3.98</td>
<td>used for Scenario CO$_2$Lo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.47x10^{11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>'x1': 1.25x10$^{12}$ mol FeS$_2$ yr$^{-1}$</td>
<td>+0.28  +3.09  +2.92</td>
<td></td>
<td>-485</td>
<td>-3.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>'x2': 2.5x10$^{12}$ mol FeS$_2$ yr$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S9 Summary of pH rise mechanisms included in scenarios $CO_2Hi$ and $CO_2Lo$

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$CO_2Hi$</th>
<th>$CO_2Lo$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease in calcification</td>
<td>$k_{\text{carbsedshallow}}$ decrease from 1.8433 x 10^{13}$ to 0.72 x 10^{12}$</td>
<td>$k_{\text{carbsedshallow}}$ decrease from 1.44 x 10^{12}$ to 2.47 x 10^{11}$</td>
</tr>
<tr>
<td>Productivity, anoxia</td>
<td>Increase P linearly to 2.3x, over interval 252.25 – 252.05 Ma</td>
<td></td>
</tr>
<tr>
<td>Pyrite burial</td>
<td>1.25 x 10^{12} mol FeS$_2$ yr$^{-1}$ starting at 252.05 Ma</td>
<td></td>
</tr>
<tr>
<td>Carbonate weathering</td>
<td>9.7 x 10^{12} mol/yr starting at 251.95 Ma</td>
<td></td>
</tr>
</tbody>
</table>
6.2 Sources of carbon and volatiles causing a negative $\delta^{13}C$ excursion or pH excursion

6.2.1 Terrestrial Carbon burial

The effect of destruction of the land biota and a corresponding decline in land organic carbon burial at the PT boundary was first considered by Broecker and Peacock (89). We represent this by setting land organic carbon burial to zero at $T=251.95$Ma, resulting in a drop in $\delta^{13}C_{\text{carb}}$ of $\approx 4\%$ (comparable to that seen in end-Permian sections), but over timescale of $\sim 100$kyr.

6.2.2 Marine Carbon burial

Despite (or because of) ecological shifts to a cyanobacteria dominated ecosystem (3), proxy evidence for continued high sediment organic carbon fluxes (84) and a vertical $\delta^{13}C$ gradient (92, 93) as well as continuing marine anoxia suggests that high marine productivity continues through Permian-Triassic. Interruption to the marine biological pump would result in a short timescale (ocean circulation timescale $\sim 10^3$ yr) increase in surface ocean pH and decrease in surface ocean (and hence carbonate) $\delta^{13}C$. This was considered as a mechanism for short-timescale $\delta^{13}C$ fluctuations over the PT interval (67). We do not consider this further here as this mechanism results in coupled perturbations to both surface ocean pH and $\delta^{13}C$, and hence cannot be the major driver for the ‘$\delta^{13}C$ without pH’ or ‘pH without $\delta^{13}C$’ signals. Smaller perturbations (interruptions) to the biological pump may be plausible as a contributor to short-timescale $\delta^{13}C$ signals following EP1.
6.2.3 Siberian traps volcanism and contact metamorphism

In order to bound plausible model scenarios, we review here potential mechanisms for volatile input from the Siberian Traps and summarise constraints on magnitudes and rates, based on (24, 27, 93).

The Siberian Traps magma area is estimated as 2.5 – 5x10^6 km^2 and volume > 2x10^6 km^3. This intruded into the Tungska sedimentary sequence, which reaches 12.5 km in thickness and includes. ≈2.5 km of Cambrian evaporites containing abundant limestone, halite, dolomite and anhydrite (24, 27), coal deposits, as well as Neo-Proterozoic petroleum-bearing shale and carbonate. Intrusion of magma into the sediments resulted in abundant sills and dykes with accompanying contact aureoles, and explosively-generated pipes. The igneous province is estimated to contain approximately 50% intrusive dykes and sills, 30% basalt lava flows, and 20% pyroclastic material (94, 95).

The volume of sediments affected by contact metamorphism is estimated (27) from a sill area of 2x10^6 km^2, thickness 200m, generating a contact aureole of thickness 400m. This results in potential release of 0.8-2.3x10^{18} mol C (as isotopically light methane and CO_2) from metamorphic degassing of organic carbon (assuming the TOC weight percent reacted is 0.5 – 1.5%), over a timescale ≈50kyr. In addition, pipes (each with source region ≈5 km^3) could release 0.1 – 0.3x10^{18} mol C over ≈6.5 kyr. Intrusion into carbonates could release comparable quantities of isotopically-heavy CO_2 via calcsilicate formation and decarbonation of dolomite into periclase and calcite, and intrusion into anhydrite could release comparable quantities of S as SO_2 (96). Interaction between petroleum-bearing inclusions and host rock salt could in addition generate halocarbons, estimated at 1-3x10^{17}.
mol CH$_3$Cl (35). Intrusion into coal-seams could result in explosive interaction resulting in large-scale coal combustion (93).

The Siberian Traps magmas contain anomalously high quantities of S, Cl, F (27), estimated to result in total intrusive and extrusive degassing of 0.2-0.25x10$^{18}$ mol S, 0.1-0.25 x10$^{18}$ mol Cl, and 0.4-0.7 x10$^{18}$ mol F (31). The ultimate source of these volatiles is likely to be assimilation from sedimentary host rocks.

6.2.4 Carbon injection perturbations

Given the episodic nature and likely variability in isotopic composition of carbon additions from Siberian Traps volcanism and contact metamorphism, we consider size, rate, and isotopic composition of carbon additions via sensitivity studies within plausible ranges.

The effect on $\delta^{13}$C$_{carb}$ of a carbon addition of isotopic composition $\delta^{13}$C$_{carb}$ is given approximately by mass-balance with the surface (atmosphere and ocean) carbon reservoirs (78, 79). The effect on pH is additionally dependent on the rate of addition. We show in Table S10 model results for combinations of addition size, isotopic composition and rate, constrained to result in $\delta^{13}$C$_{carb}$ = -3 ‰, demonstrating the additional non-linear effect of land-surface weathering feedbacks (‘land carbonate compensation’).

The decline in $\delta^{13}$C$_{carb}$ over the P-T boundary is faster than can be accounted for by a decrease in land carbon burial alone, implying an additional pulse of isotopically light carbon contribution $\sim$2‰ to the decline. We show in Figure S7 the constraints from the $\delta^{11}$B data on carbon additions over the 50kyr interval 251.95 – 251.90 Ma. The results demonstrate that providing the rate of carbon addition is relatively slow as here, the pH
constraints are in fact relatively weak, and are consistent with a range of input isotopic compositions $\delta^{13}C_{inj}$.

Table S10 Carbon injection perturbations, constrained to result in $\delta^{13}C_{carb} = -3 \%o$ when applied to steady-state condition CO$_2$Lo.

<table>
<thead>
<tr>
<th>Size (mol C)</th>
<th>Duration (yr)</th>
<th>Rate (mol / yr)</th>
<th>$\delta^{13}C_{inj}$</th>
<th>$\Delta$ pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.75 x 10$^{17}$</td>
<td>10$^3$ yr</td>
<td>4.75 x 10$^{12}$</td>
<td>-50</td>
<td>-0.07</td>
</tr>
<tr>
<td>2.47 x 10$^{18}$</td>
<td>10$^3$ yr</td>
<td>2.47 x 10$^{13}$</td>
<td>-10</td>
<td>-0.28</td>
</tr>
<tr>
<td>3.32 x 10$^{17}$</td>
<td>10$^4$ yr</td>
<td>3.32 x 10$^{13}$</td>
<td>-50</td>
<td>-0.18</td>
</tr>
<tr>
<td>1.75 x 10$^{18}$</td>
<td>10$^4$ yr</td>
<td>1.75 x 10$^{14}$</td>
<td>-10</td>
<td>-0.64</td>
</tr>
</tbody>
</table>

The acidification event at ~251.89Ma requires a rapid addition of carbon on a timescale $\leq$ 10 kyr, with an isotopic composition $\delta^{13}C_{inj} \approx 0 \%o$ in order to leave $\delta^{13}C_{carb}$ unaffected, and size $\geq 2 \times 10^{18}$ mol in order to produce a sufficient decline in pH and $\delta^{11}B$ (Figure S8). Larger (or more rapid) carbon additions produce relatively little additional response in ocean pH, as the majority of the input carbon remains in the atmosphere, and the response of the $\delta^{11}B$ is also non-linear at low pH. The rate of the inferred carbon addition is $\sim$3 times the estimates above for organic carbon from the combined effects of sills (0.16 – 0.4 $\times 10^{18}$ mol C over 10 kyr) and pipes (0.1 – 0.3 $\times 10^{18}$ mol C over $\sim 6.5$ kyr), but is not unreasonable given the carbonate carbon source and large uncertainties in these estimates.

6.2.5 SO$_2$ injection perturbation

Contact metamorphism of evaporites resulting in large SO$_2$ release could potentially also contribute to the acidification event. Quantitatively the effect (per mol) on ocean pH is
approximately twice that of a carbon addition, and given the relative abundance of evaporites to carbonates is therefore likely to represent a smaller contribution to acidification.
Figure S7 Effect of changing size and isotopic composition of CO₂ input perturbations applied to scenario CO₂Hi over 50kyr interval 251.95 – 251.90 Ma. 'land only' shows the effect of interruption in land organic burial, '0.32 -50 only' shows the effect of carbon addition only. Other lines show combined effect of land burial and carbon addition. Perturbations are constructed to result in $\delta^{13}C_{\text{carb}} \approx -2 \%_0$, and correspond to inputs of: 0.32x$10^{18}$ mol / -50 \%$_0$; 0.65x$10^{18}$ mol / -25 \%$_0$; 1.30x$10^{18}$ mol / -12.5 \%$_0$
Figure S8 Effect of changing size of CO$_2$ input perturbations applied to scenarios CO2Hi and CO2Lo over 10kyr interval 251.89 – 251.88 Ma. Perturbation sizes are 2x10$^{18}$ mol and 4x10$^{18}$ mol. Isotopic composition is 2.65 ‰, ie equal to that of sedimentary carbonate.
Figure S9 Additional model output for CO$_2$ scenarios shown in main paper Figure 3. Weathering fluxes are shown for scenario CO$_2$Lo only.