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# **Title: Ocean Acidification and the Permo-Triassic Mass Extinction**

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**Abstract:** Ocean acidification triggered by Siberian Trap volcanism was a possible kill mechanism for the Permian Triassic Boundary (PTB) mass extinction, but direct evidence for an acidification event is lacking. 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, increased ocean alkalinity, primed the Earth system with a low level of

atmospheric CO<sub>2</sub> and a high ocean buffering capacity. The first phase of extinction was coincident with a slow injection of carbon into the atmosphere and ocean pH remained stable. During the second extinction pulse, however, a rapid and large injection of carbon caused an abrupt 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 PTB extinction event spanned ~60 thousand years (2) and can be resolved into two distinct marine extinction pulses (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 CO<sub>2</sub> 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 interval (10, 11). The interpretation of these records is, however, debated (12-16), and is of great importance to understanding the current threat of anthropogenically-driven ocean acidification (11).

To test the ocean acidification hypothesis we have constructed a proxy record of ocean pH across the PTB, using the boron isotope composition of marine carbonates ( $\delta^{11}\text{B}_{\text{carb}}$ ) (17). We then employ a carbon cycle model (*supplementary online text*) to explore ocean carbonate chemistry and pH scenarios that are consistent with our  $\delta^{11}\text{B}$  data and published records of carbon cycle disturbance and environmental conditions. 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 and carbon 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  $\delta^{13}\text{C}_{\text{carb}}$  are well constrained (18). During the PTB interval the U.A.E. formed an expansive carbonate platform that remained connected to the central Neo-Tethyan Ocean (15) (Fig 1A). Conodont stratigraphy and the distinct  $\delta^{13}\text{C}_{\text{carb}}$  curve are used to constrain the age model (17).

The run-up to PTB in the Tethys is characterized by two negative  $\delta^{13}\text{C}$  excursions interrupted by a short-term positive event (10). There is no consensus as to the cause of this rebound event and so we instead focus on the broader  $\delta^{13}\text{C}$  trend. Our  $\delta^{13}\text{C}$  transect (Fig. 1B) starts in the Changhsingian (Late Permian) with a gradual decreasing trend, interrupted by the first negative shift in  $\delta^{13}\text{C}$  at EP1 (at 53 m, ~251.96 Ma, Fig. 1B and 2). This is followed by the minor positive ‘rebound’ event (at 54 m, ~251.95 Ma, Fig. 1B and 2) prior to the minima of the second phase of the negative CIE (58-60 m, ~251.92 Ma, Figs. 1B and 2) that marks the PTB itself. After the CIE minimum,  $\delta^{13}\text{C}$  gradually increases to ~1.8‰ and remains relatively stable during the earliest Triassic and across EP2.

Our boron isotope record shows a different pattern to the carbon isotope excursion.  $\delta^{11}\text{B}$  is persistently low (Fig. 1C) at the start of our record during the late-Changhsingian, with an average of  $10.9 \pm 0.9\text{‰}$  ( $1\sigma$ ). This is in agreement with  $\delta^{11}\text{B}$  values (average of  $10.6 \pm 0.6\text{‰}$ ,  $1\sigma$ ) reported for early-Permian brachiopods (19). Further up section (at ~40 m, ~252.04 Ma, Fig. 1C), there is a stepped increase in  $\delta^{11}\text{B}$  to  $15.3 \pm 0.8\text{‰}$  (average  $\pm 2\sigma$ ), and by implication an increase in ocean pH of ~0.4-0.5 units (Fig. 2).  $\delta^{11}\text{B}$  values then remain relatively stable, scattering around  $14.8 \pm 1.0\text{‰}$  ( $1\sigma$ ) 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. 1 and 2).

After the  $\delta^{13}\text{C}$  increase and stabilization (at ~85 m, ~251.88 Ma, Fig. 1),  $\delta^{11}\text{B}$  begins to decrease rapidly to  $8.2 \pm 1.2\text{‰}$  ( $2\sigma$ ), implying a sharp drop in pH of ~0.6-0.7 units. The  $\delta^{11}\text{B}$  minimum is coincident with the interval identified as EP2. This ocean acidification event is short-lived (~10 thousand years) and  $\delta^{11}\text{B}$  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. 2) suggests a large increase in carbonate alkalinity (20). We are able to simulate the observed rise in  $\delta^{11}\text{B}$  and pH through different model combinations of increasing silicate weathering, increased pyrite deposition (21), an increase in carbonate weathering, and a decrease in shallow marine carbonate depositional area (supplementary online text). Both silicate weathering and pyrite deposition result in a large drop in  $p\text{CO}_2$  (and temperature) for a given increase in pH and saturation state ( $\Omega$ ). There is no evidence for a large drop in  $p\text{CO}_2$ , and independent proxy data indicate only a minor temperature decrease of a few degrees C during the Changhsingian (22), suggesting that these mechanisms alone cannot explain the pH increase (Fig. S5). 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  $p\text{CO}_2$  and temperature (Fig. S6).

A decrease in carbonate sedimentation is consistent with the decrease in depositional shelf area that occurred due to the 2<sup>nd</sup> order regression of the Late Permian (23). With the added expansion of anoxia into shelf environments (24), 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 (23), which would have further augmented the alkalinity influx. The pH increase event supports the  $\text{CO}_2\text{Lo}$  initialization scenario (*supplementary online text*;  $\text{CO}_2 \sim 3$  PAL (Present Atmospheric Levels), pH  $\sim 8$ ,  $\delta^{11}\text{B}_{\text{sw}} \sim 34\text{‰}$ ) as the simulated  $\text{CO}_2$  and temperature decrease is much reduced, and therefore more consistent with independent proxy data (22), compared to  $\text{CO}_2\text{Hi}$  ( $\text{CO}_2 \sim 10$  PAL, pH  $\sim 7.5$ ,  $\delta^{11}\text{B}_{\text{sw}} \sim 36.8\text{‰}$ ) (Fig. 2D).

Prior to EP1,  $\delta^{13}\text{C}_{\text{carb}}$  values began to decrease before reaching the minimum of the globally recognized negative CIE at the PTB (Fig. 1). At this time both  $\delta^{11}\text{B}$  and ocean pH remained stable. Hypotheses to explain the negative CIE require the input of isotopically light carbon, such as from volcanism (14, 25) with the assimilation of very light organic carbon from the surrounding host rock (26), methane destabilization (27), collapse of the biological pump (15), and/or a decrease in the burial of terrestrial carbon (16). We can simulate the observed drop in  $\delta^{13}\text{C}_{\text{carb}}$ , whilst remaining within the uncertainty of the  $\delta^{11}\text{B}$  data (Fig. 2), by combining a cessation of terrestrial carbon burial with a relatively slow (50 thousand years) carbon injection from any of the above sources (Fig. S8). A small source of methane ( $3.2 \times 10^{17}$  mol C with  $\delta^{13}\text{C} = -50\text{‰}$ ) gives the least change in  $\delta^{11}\text{B}$  and pH, whilst either a larger source of organic carbon ( $\sim 6.5 \times 10^{17}$  mol C with  $\delta^{13}\text{C} = -25\text{‰}$ ) or a mixture of mantle and lighter carbon sources ( $\sim 1.3 \times 10^{18}$  mol C with  $\delta^{13}\text{C} = -12.5\text{‰}$ ) are still within the measured uncertainty in  $\delta^{11}\text{B}$ .

124           This relatively slow addition of carbon minimizes the tendency for a transient decline  
125 in surface ocean pH in an ocean that was already primed with a high  $\Omega$  and hence high  
126 buffering capacity from the Late Permian. The global presence of microbial and abiotic  
127 carbonate fabrics after EP1 (28) are indicative that this high  $\Omega$  was maintained across the  
128 CIE. The carbon injection triggers an increase in  $p\text{CO}_2$ , temperature and silicate weathering,  
129 thereby creating an additional counterbalancing alkalinity flux, which is consistent with  
130 independent proxy data (6). The alkalinity source may have been further increased through  
131 soil loss (29), the emplacement of easily-weathered Siberian Trap basalt, or the impact of  
132 acid rain (30) that would have increased weathering efficiency.

133           The negative  $\delta^{11}\text{B}_{\text{carb}}$  excursion at 251.88 Ma represents a calculated pH decrease of  
134 up to 0.7 pH units. This pH decrease coincides with the second pulse of the extinction (Fig.  
135 1), which preferentially affected the heavily calcifying, physiologically un-buffered and  
136 sessile organisms (3). This was also accompanied by the temporary loss of abiotic and  
137 microbial carbonates throughout the Tethys (31, 32), thereby suggesting a coeval decrease in  
138  $\Omega$ . To overwhelm the buffering capacity of the ocean and decrease pH in this way requires a  
139 second, more abrupt injection of carbon into the atmosphere, yet remarkably, the acidification  
140 event occurs after the decline in  $\delta^{13}\text{C}$ , when  $\delta^{13}\text{C}$  has rebounded somewhat and is essentially  
141 stable (Fig. 1).

142           Unlike the first carbon injection, the lack of change in  $\delta^{13}\text{C}$  at this time rules out very  
143  $^{13}\text{C}$ -depleted carbon sources, because no counterbalancing strongly  $^{13}\text{C}$ -enriched source  
144 exists. Instead, it requires a carbon source near  $\sim 0\text{‰}$ . A plausible scenario for this is the  
145 decarbonation of overlying carbonate host rock, into which the Siberian Traps intruded (26)  
146 or the direct assimilation of carbonates and evaporites into the melt (33). Host carbonates  
147 would have had  $\delta^{13}\text{C} \sim +2\text{--}4\text{‰}$ , which when mixed with mantle carbon ( $\sim -5\text{‰}$ ), potentially  
148 produces a source near  $0\text{‰}$ . We can simulate the sharp drop in pH and stable  $\delta^{13}\text{C}$  values

(Fig. 2) through a large and rapid carbon release of  $2 \times 10^{18}$  mol C over 10 thousand years (Fig. S8). This is undoubtedly a massive injection of 24,000 PgC at a rapid rate of 2.4 PgC/yr, but it is physically plausible given existing estimates of the volume of carbonate host sediments subject to contact metamorphism and postulated mechanisms of carbon release (*supplementary online text*). This second rapid carbon release produces a sharp rise in  $p\text{CO}_2$  to ~20 PAL and warming of ~15°C, consistent with the observation of peak temperatures after EP1 (22). Initialization of the carbon cycle model under  $\text{CO}_2\text{Hi}$  cannot generate the magnitude of  $\delta^{11}\text{B}$  drop (Fig. 2A) because the non-linear relation between pH and  $\delta^{11}\text{B}$  fractionation sets a lower limit of  $\delta^{11}\text{B}$  at ~10‰ in this case (Fig. S3). Thus low initial  $\text{CO}_2$  of ~3 PAL in the late Permian ( $\text{CO}_2\text{Lo}$ ) is more consistent with our data.

An acidification event of ~10 thousand years is consistent with the modelled timescale required to replenish the ocean with alkalinity, as carbonate deposition is reduced and weathering is increased under higher  $p\text{CO}_2$  and global temperatures. Increased silicate weathering rates drive further  $\text{CO}_2$  drawdown resulting in stabilization (Fig. S7). High global temperature (6) and increased silicate weathering are consistent with a sudden increase in both  $^{87}\text{Sr}/^{86}\text{Sr}$  (34) and sedimentation rates (29) in the Griesbachian.

The PTB was a time of extreme environmental change, and our combined data and modeling approach falsifies several of the mechanisms currently proposed. Whilst the coincident stresses of anoxia, increasing temperature, and ecosystem restructuring were important during this interval, the  $\delta^{11}\text{B}$  record strongly suggests that widespread ocean acidification was not a factor in the first phase of the mass extinction, but did drive the second pulse. The carbon release required to drive the observed acidification event must have occurred at a rate comparable to the current anthropogenic perturbation, but exceeds it in expected magnitude. Specifically, the required model perturbation of 24,000 PgC exceeds the ~5000 PgC of conventional fossil fuels and is at the upper end of the range of estimates of



174 unconventional fossil fuels (e.g. methane hydrates). We show that such a rapid and large  
175 release of carbon is critical to causing the combined synchronous decrease in both pH and  
176 saturation state that defines an ocean acidification event (*II*).

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238 21. Bacterial Sulfate Reduction (BSR) is a net source of alkalinity if the generated  $\text{H}_2\text{S}$  is  
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**Fig. 1.** Site locality and high resolution carbon and boron isotope data. **(A)** Paleogeographic reconstruction for the Late Permian showing the studied section Wadi Bih, in the Musandam Mountains of U.A.E. that formed an extensive carbonate platform in the Neo-Tethyan Ocean. Modified from (35). **(B)** Shallow water  $\delta^{13}\text{C}$  record (18). **(C)** Boron isotope ( $\delta^{11}\text{B}$ ) record (propagated uncertainty given as  $2\sigma_f$ ) and average Early Permian brachiopod value ( $n=5$ ) (19). See **(A)** for lithology, biota and transect key. Only *Hindeodus parvus* has been found so far in this section and the conodont zones with dashed line are identified from the  $\delta^{13}\text{C}$  record (36-38).

**Fig. 2.** Model results of carbon cycle parameters for the two end-member  $\text{CO}_2$  scenarios;  $\text{CO}_2\text{Hi}$  and  $\text{CO}_2\text{Lo}$  (17). **(A)** Model reproduced  $\delta^{11}\text{B}$  vs data. **(B)** Modelled  $\delta^{13}\text{C}$  vs data. **(C)** Modelled pH envelope incorporating uncertainty of seawater B isotope composition ( $\delta^{11}\text{B}_{\text{sw}}$ ) and dynamic temperatures. **(D)** Calculated atmospheric  $\text{CO}_2$ .

**Supplementary Materials:**

Materials and Methods

Supplementary Text

Figures S1-S9

Tables S1-S10

References (39-100)