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

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20

21 **Abstract:** Ocean acidification triggered by Siberian Trap volcanism was a possible kill
22 mechanism for the Permian Triassic Boundary (PTB) mass extinction, but direct evidence for
23 an acidification event is lacking. We present a high resolution seawater pH record across this
24 interval, utilizing boron isotope data combined with a quantitative modeling approach. In the
25 latest Permian, increased ocean alkalinity, primed the Earth system with a low level of

26 atmospheric CO₂ and a high ocean buffering capacity. The first phase of extinction was
27 coincident with a slow injection of carbon into the atmosphere and ocean pH remained stable.
28 During the second extinction pulse, however, a rapid and large injection of carbon caused an
29 abrupt acidification event that drove the preferential loss of heavily calcified marine biota.

30

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

34

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

44 Models of PTB ocean acidification suggest that a massive, and rapid, release of CO₂ from
45 Siberian Trap volcanism, acidified the ocean (7). Indirect evidence for acidification comes
46 from the interpretation of faunal turnover records (3, 8), potential dissolution surfaces (9) and
47 Ca isotope data (7). A rapid input of carbon is also potentially recorded in the negative
48 carbon isotope excursion (CIE) that characterizes the PTB interval (10, 11). The
49 interpretation of these records is, however, debated (12-16), and is of great importance to
50 understanding the current threat of anthropogenically-driven ocean acidification (11).

51 To test the ocean acidification hypothesis we have constructed a proxy record of
52 ocean pH across the PTB, using the boron isotope composition of marine carbonates
53 ($\delta^{11}\text{B}_{\text{carb}}$) (17). We then employ a carbon cycle model (*supplementary online text*) to explore
54 ocean carbonate chemistry and pH scenarios that are consistent with our $\delta^{11}\text{B}$ data and
55 published records of carbon cycle disturbance and environmental conditions. Through this
56 combined geochemical, geological and modelling approach we are able to produce an
57 envelope that encompasses the most realistic range in pH, which then allows us to resolve
58 three distinct chronological phases of carbon cycle perturbation, each with very different
59 environmental consequences for the Late Permian-Early Triassic Earth system.

60 We analyzed boron and carbon isotope data from two complementary transects in a
61 shallow marine, open water carbonate succession from the United Arab Emirates (U.A.E.),
62 where depositional facies and $\delta^{13}\text{C}_{\text{carb}}$ are well constrained (18). During the PTB interval the
63 U.A.E. formed an expansive carbonate platform that remained connected to the central Neo-
64 Tethyan Ocean (15) (Fig 1A). Conodont stratigraphy and the distinct $\delta^{13}\text{C}_{\text{carb}}$ curve are used
65 to constrain the age model (17).

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

75 Our boron isotope record shows a different pattern to the carbon isotope excursion. $\delta^{11}\text{B}$
76 is persistently low (Fig. 1C) at the start of our record during the late-Changhsingian, with an
77 average of $10.9 \pm 0.9\text{‰}$ (1σ). This is in agreement with $\delta^{11}\text{B}$ values (average of $10.6 \pm 0.6\text{‰}$,
78 1σ) reported for early-Permian brachiopods (19). Further up section (at ~40 m, ~252.04 Ma,
79 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
80 implication an increase in ocean pH of ~0.4-0.5 units (Fig. 2). $\delta^{11}\text{B}$ values then remain
81 relatively stable, scattering around $14.8 \pm 1.0\text{‰}$ (1σ) and implying variations within 0.1-0.2
82 pH units, into the Early Griesbachian (Early Triassic) and hence across EP1 and the period of
83 carbon cycle disturbance (Figs. 1 and 2).

84 After the $\delta^{13}\text{C}$ increase and stabilization (at ~85 m, ~251.88 Ma, Fig. 1), $\delta^{11}\text{B}$ begins
85 to decrease rapidly to $8.2 \pm 1.2\text{‰}$ (2σ), implying a sharp drop in pH of ~0.6-0.7 units. The
86 $\delta^{11}\text{B}$ minimum is coincident with the interval identified as EP2. This ocean acidification
87 event is short-lived (~10 thousand years) and $\delta^{11}\text{B}$ values quickly recover toward the more
88 alkaline values evident during EP1 (average of ~14‰).

89 The initial rise in ocean pH of ~0.4-0.5 units during the Late Permian (Fig. 2)
90 suggests a large increase in carbonate alkalinity (20). We are able to simulate the observed
91 rise in $\delta^{11}\text{B}$ and pH through different model combinations of increasing silicate weathering,
92 increased pyrite deposition (21), an increase in carbonate weathering, and a decrease in
93 shallow marine carbonate depositional area (supplementary online text). Both silicate
94 weathering and pyrite deposition result in a large drop in $p\text{CO}_2$ (and temperature) for a given
95 increase in pH and saturation state (Ω). There is no evidence for a large drop in $p\text{CO}_2$, and
96 independent proxy data indicate only a minor temperature decrease of a few degrees C during
97 the Changhsingian (22), suggesting that these mechanisms alone cannot explain the pH
98 increase (Fig. S5). Conversely, an increase in carbonate input or a reduction in rates of

99 carbonate deposition both result in increases in Ω , with a greater impact on pH per unit
100 decrease in $p\text{CO}_2$ and temperature (Fig. S6).

101 A decrease in carbonate sedimentation is consistent with the decrease in depositional
102 shelf area that occurred due to the 2nd order regression of the Late Permian (23). With the
103 added expansion of anoxia into shelf environments (24), this would effectively create both
104 bottom-up and top-down pressures to reduce the area of potential carbonate sedimentation.
105 Sea level fall also exposed carbonates to weathering (23), which would have further
106 augmented the alkalinity influx. The pH increase event supports the CO_2Lo initialization
107 scenario (*supplementary online text*; $\text{CO}_2 \sim 3$ PAL (Present Atmospheric Levels), pH ~ 8 ,
108 $\delta^{11}\text{B}_{\text{Sw}} \sim 34\text{‰}$) as the simulated CO_2 and temperature decrease is much reduced, and
109 therefore more consistent with independent proxy data (22), compared to CO_2Hi ($\text{CO}_2 \sim 10$
110 PAL, pH ~ 7.5 $\delta^{11}\text{B}_{\text{Sw}} \sim 36.8\text{‰}$) (Fig. 2D).

111 Prior to EP1, $\delta^{13}\text{C}_{\text{carb}}$ values began to decrease before reaching the minimum of the
112 globally recognized negative CIE at the PTB (Fig. 1). At this time both $\delta^{11}\text{B}$ and ocean pH
113 remained stable. Hypotheses to explain the negative CIE require the input of isotopically light
114 carbon, such as from volcanism (14, 25) with the assimilation of very light organic carbon
115 from the surrounding host rock (26), methane destabilization (27), collapse of the biological
116 pump (15), and/or a decrease in the burial of terrestrial carbon (16). We can simulate the
117 observed drop in $\delta^{13}\text{C}_{\text{carb}}$, whilst remaining within the uncertainty of the $\delta^{11}\text{B}$ data (Fig. 2), by
118 combining a cessation of terrestrial carbon burial with a relatively slow (50 thousand years)
119 carbon injection from any of the above sources (Fig. S8). A small source of methane (3.2
120 $\times 10^{17}$ mol C with $\delta^{13}\text{C} = -50\text{‰}$) gives the least change in $\delta^{11}\text{B}$ and pH, whilst either a larger
121 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
122 lighter carbon sources ($\sim 1.3 \times 10^{18}$ mol C with $\delta^{13}\text{C} = -12.5\text{‰}$) are still within the measured
123 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 Ω 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 Ω 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 Ω . 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}C -depleted carbon sources, because no counterbalancing strongly ^{13}C -enriched source
144 exists. Instead, it requires a carbon source near $\sim 0\%$. 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 $\delta^{13}\text{C} \sim +2\text{-}4\%$, which when mixed with mantle carbon ($\sim -5\%$), potentially
148 produces a source near 0% . We can simulate the sharp drop in pH and stable $\delta^{13}\text{C}$ values

149 (Fig. 2) through a large and rapid carbon release of 2×10^{18} mol C over 10 thousand years (Fig.
150 S8). This is undoubtedly a massive injection of 24,000 PgC at a rapid rate of 2.4 PgC/yr, but
151 it is physically plausible given existing estimates of the volume of carbonate host sediments
152 subject to contact metamorphism and postulated mechanisms of carbon release
153 (*supplementary online text*). This second rapid carbon release produces a sharp rise in $p\text{CO}_2$
154 to ~20 PAL and warming of ~15°C, consistent with the observation of peak temperatures
155 after EP1 (22). Initialization of the carbon cycle model under CO_2Hi cannot generate the
156 magnitude of $\delta^{11}\text{B}$ drop (Fig. 2A) because the non-linear relation between pH and $\delta^{11}\text{B}$
157 fractionation sets a lower limit of $\delta^{11}\text{B}$ at ~10‰ in this case (Fig. S3). Thus low initial CO_2 of
158 ~3 PAL in the late Permian (CO_2Lo) is more consistent with our data.

159 An acidification event of ~10 thousand years is consistent with the modelled
160 timescale required to replenish the ocean with alkalinity, as carbonate deposition is reduced
161 and weathering is increased under higher $p\text{CO}_2$ and global temperatures. Increased silicate
162 weathering rates drive further CO_2 drawdown resulting in stabilization (Fig. S7). High global
163 temperature (6) and increased silicate weathering are consistent with a sudden increase in
164 both $^{87}\text{Sr}/^{86}\text{Sr}$ (34) and sedimentation rates (29) in the Griesbachian.

165 The PTB was a time of extreme environmental change, and our combined data and
166 modeling approach falsifies several of the mechanisms currently proposed. Whilst the
167 coincident stresses of anoxia, increasing temperature, and ecosystem restructuring were
168 important during this interval, the $\delta^{11}\text{B}$ record strongly suggests that widespread ocean
169 acidification was not a factor in the first phase of the mass extinction, but did drive the
170 second pulse. The carbon release required to drive the observed acidification event must have
171 occurred at a rate comparable to the current anthropogenic perturbation, but exceeds it in
172 expected magnitude. Specifically, the required model perturbation of 24,000 PgC exceeds the
173 ~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*).

177

178

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482

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494

495 **Fig. 1.** Site locality and high resolution carbon and boron isotope data. **(A)** Paleogeographic
496 reconstruction for the Late Permian showing the studied section Wadi Bih, in the Musandam
497 Mountains of U.A.E. that formed an extensive carbonate platform in the Neo-Tethyan Ocean.
498 Modified from (35). **(B)** Shallow water $\delta^{13}\text{C}$ record (18). **(C)** Boron isotope ($\delta^{11}\text{B}$) record
499 (propagated uncertainty given as $2\sigma_f$) and average Early Permian brachiopod value (n=5)
500 (19). See **(A)** for lithology, biota and transect key. Only *Hindeodus parvus* has been found so
501 far in this section and the conodont zones with dashed line are identified from the $\delta^{13}\text{C}$ record
502 (36-38).

503

504 **Fig. 2.** Model results of carbon cycle parameters for the two end-member CO_2 scenarios;
505 CO_2Hi and CO_2Lo (17). **(A)** Model reproduced $\delta^{11}\text{B}$ vs data. **(B)** Modelled $\delta^{13}\text{C}$ vs data. **(C)**
506 Modelled pH envelope incorporating uncertainty of seawater B isotope composition ($\delta^{11}\text{B}_{\text{sw}}$)
507 and dynamic temperatures. **(D)** Calculated atmospheric CO_2 .

508 **Supplementary Materials:**

509 Materials and Methods

510 Supplementary Text

511 Figures S1-S9

512 Tables S1-S10

513 References (39-100)