Ocean Acidification and the Permo-Triassic Mass Extinction

Citation for published version:
Clarkson, MO, Kasemann, S, Wood, R, Lenton, TM, Daines, SJ, Richoz, S, Ohnemueller, F, Poulton, SW & Tipper, ET 2015, 'Ocean Acidification and the Permo-Triassic Mass Extinction', *Science*, vol. 348, no. 6321, pp. 229-232 . https://doi.org/10.1126/science.aaa0193

Digital Object Identifier (DOI):
10.1126/science.aaa0193

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Science

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Authors: Clarkson, M.O.[1*†]; Kasemann, S.A. [2]; Wood, R.[1]; Lenton, T.M.[3]; Daines, S.J.[3]; Richoz, S.[4]; Ohnemueller, F.[2]; Meixner, A.[2]; Poulton, S.W.[5] and Tipper, E.T.[6]

Affiliations:

[1.] School of Geosciences, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JW, UK

[2.] Faculty of Geosciences and MARUM-Center for Marine Environmental Sciences, University of Bremen, 28334 Bremen, Germany

[3.] College of Life and Environmental Sciences, University of Exeter, Laver Building, North Parks Road, Exeter, EX4 4QE, UK.

[4.] Institute of Earth Sciences, NAWI Graz, University of Graz, Heinrichstraße 26, 8010 Graz, Austria

[5.] School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

[6.] Dept. of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

*Correspondence to: matthew.clarkson@otago.ac.nz

[†]Current address: Department of Chemistry, University of Otago, Union Street, Dunedin, 9016, PO Box 56, New Zealand.

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_2 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_2 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 ($\delta^{11}B_{carb}$) (*17*). We then employ a carbon cycle model (*supplementary online text*) to explore ocean carbonate chemistry and pH scenarios that are consistent with our $\delta^{11}B$ 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 $\delta^{13}C_{carb}$ 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 $\delta^{13}C_{carb}$ curve are used to constrain the age model (17).

The run-up to PTB in the Tethys is characterized by two negative $\delta^{13}C$ 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 $\delta^{13}C$ trend. Our $\delta^{13}C$ transect (Fig. 1B) starts in the Changhsingian (Late Permian) with a gradual decreasing trend, interrupted by the first negative shift in $\delta^{13}C$ 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, $\delta^{13}C$ 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. $\delta^{11}B$ is persistently low (Fig. 1C) at the start of our record during the late-Changhsingian, with an average of 10.9 ± 0.9‰ (1σ). This is in agreement with $\delta^{11}B$ values (average of 10.6 ± 0.6‰, 1σ) reported for early-Permian brachiopods (*19*). Further up section (at ~40 m, ~252.04 Ma, Fig. 1C), there is a stepped increase in $\delta^{11}B$ to 15.3±0.8‰ (average ± 2σf), and by implication an increase in ocean pH of ~0.4-0.5 units (Fig. 2). $\delta^{11}B$ values then 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. 1 and 2).

After the $\delta^{13}C$ increase and stabilization (at ~85 m, ~251.88 Ma, Fig. 1), $\delta^{11}B$ begins to decrease rapidly to 8.2±1.2‰ (2σf), implying a sharp drop in pH of ~0.6-0.7 units. The $\delta^{11}B$ minimum is coincident with the interval identified as EP2. This ocean acidification event is short-lived (~10 thousand years) and $\delta^{11}B$ 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 $\delta^{11}B$ 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 pCO_2 (and temperature) for a given increase in pH and saturation state (Ω). There is no evidence for a large drop in pCO_2, and independent proxy data indicate only a minor temperature decrease of a few degrees C during the Changsingian (*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 Ω, with a greater impact on pH per unit decrease in pCO_2 and temperature (Fig. S6).

A 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 (*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 CO_2*Lo* initialization scenario (*supplementary online text*; CO_2 ~3 PAL (Present Atmospheric Levels), 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. 2D).

Prior to EP1, $\delta^{13}C_{carb}$ values began to decrease before reaching the minimum of the globally recognized negative CIE at the PTB (Fig. 1). At this time both $\delta^{11}B$ 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 $\delta^{13}C_{carb}$, whilst remaining within the uncertainty of the $\delta^{11}B$ 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 $\times10^{17}$ 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 (~6.5×10^{17} mol C with $\delta^{13}C$ = -25‰) or a mixture of mantle and lighter carbon sources (~1.3×10^{18} mol C with $\delta^{13}C$ = -12.5‰) are still within the measured uncertainty in $\delta^{11}B$.

This relatively slow addition of carbon minimizes 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 (*28*) are indicative that this high Ω was maintained across the CIE. The carbon injection triggers an increase in pCO_2, temperature and silicate weathering, thereby creating an additional counterbalancing alkalinity flux, which is consistent with independent proxy data (*6*). The alkalinity source may have been further increased through soil loss (*29*), the emplacement of easily-weathered Siberian Trap basalt, or the impact of acid rain (*30*) that would have increased weathering efficiency.

The negative $\delta^{11}B_{carb}$ excursion at 251.88 Ma represents a calculated pH decrease of up to 0.7 pH units. This pH decrease coincides with the second pulse of the extinction (Fig. 1), 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 (*31, 32*), thereby suggesting a coeval decrease in Ω. To overwhelm the buffering capacity of the ocean and decrease pH in this way requires a second, more abrupt injection of carbon into the atmosphere, yet remarkably, the acidification event occurs after the decline in $\delta^{13}C$, when $\delta^{13}C$ has rebounded somewhat and is essentially stable (Fig. 1).

Unlike the first carbon injection, the lack of change in $\delta^{13}C$ 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 (*26*) or the direct assimilation of carbonates and evaporites into the melt (*33*). Host carbonates would have had $\delta^{13}C$ ~+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 $\delta^{13}C$ values

(Fig. 2) through a large and rapid carbon release of 2×10^{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 pCO_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 CO_2*Hi* cannot generate the magnitude of $\delta^{11}B$ drop (Fig. 2A) because the non-linear relation between pH and $\delta^{11}B$ fractionation sets a lower limit of $\delta^{11}B$ at ~10‰ in this case (Fig. S3). Thus low initial CO_2 of ~3 PAL in the late Permian (CO_2*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 pCO_2 and global temperatures. Increased silicate weathering rates drive further CO_2 drawdown resulting in stabilization (Fig. S7). High global temperature (*6*) and increased silicate weathering are consistent with a sudden increase in both $^{87}Sr/^{86}Sr$ (*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 $\delta^{11}B$ 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 unconventional fossil fuels (e.g. methane hydrates). We show that such a rapid and large release of carbon is critical to causing the combined synchronous decrease in both pH and saturation state that defines an ocean acidification event (*11*).

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Acknowledgements: MOC acknowledges funding from the Edinburgh University Principal's Career Development Scholarship, the International Centre for Carbonate Reservoirs and The Marsden Fund (U001314). RW, TL and SWP acknowledge support from NERC through the 'Co-evolution of Life and the Planet' scheme (NE/I005978). TL and SD were supported by the Leverhulme Trust (RPG-2013-106). SK and AM acknowledge support from the German Research Foundation (DFG Major Research Instrumentation Program). This is a contribution to IGCP 572 with SR sponsored for fieldwork by the Austrian National Committee (Austrian Academy of Sciences) for IGCP. We are grateful to R. Newton and A. Thomas for helpful discussions, L. Krystyn for field assistance, F. Maurer for providing photomicrographs, and B. Mills for assisting with model studies. Data are available online in the Supplementary Materials and at www.pangaea.de

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 $\delta^{13}C$ record (*18*). **(C)** Boron isotope ($\delta^{11}B$) 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 $\delta^{13}C$ record (*36*-*38*).

Fig. 2. Model results of carbon cycle parameters for the two end-member CO_2 scenarios; CO_2*Hi* and CO_2*Lo* (17). **(A)** Model reproduced $\delta^{11}B$ vs data. **(B)** Modelled $\delta^{13}C$ vs data. **(C)** Modelled pH envelope incorporating uncertainty of seawater B isotope composition ($\delta^{11}B_{SW}$) and dynamic temperatures. **(D)** Calculated atmospheric CO_2.

Supplementary Materials:

Materials and Methods

Supplementary Text

Figures S1-S9

Tables S1-S10

References (39-*100*)