

1 **Permian-Triassic mass extinction pulses driven by major marine carbon cycle**
2 **perturbations**

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22 **The Permian-Triassic boundary approximately 251.9 million years ago marked**
23 **the most severe environmental crisis identified in the geological record that**
24 **dictated the onwards course for the evolution of life. Magmatism from Siberian**
25 **Traps is thought to have played a significant role, but the causational trigger and**

26 **its feedbacks are yet to be fully understood. Here, we present a new boron isotope-**
27 **derived seawater pH record from fossil brachiopod shells deposited on the Tethys**
28 **shelf that demonstrates a substantial decline in seawater pH coeval with the onset**
29 **of the mass extinction in the latest Permian. Combined with carbon isotope data,**
30 **our results are integrated in a geochemical model that resolves the carbon cycle**
31 **dynamics as well as ocean redox conditions and nitrogen isotope turnover. We find**
32 **that the initial ocean acidification was intimately linked to a large pulse of carbon**
33 **degassing from the Siberian sill intrusions. We unravel the consequences of the**
34 **greenhouse effect on the marine environment, and show how elevated sea surface**
35 **temperatures, export production and nutrient input driven by increased rates of**
36 **chemical weathering gave rise to widespread de-oxygenation and sporadic**
37 **sulphide poisoning of the oceans in the earliest Triassic. Our findings enable us to**
38 **assemble a consistent biogeochemical reconstruction of the mechanisms resulting**
39 **in the largest Phanerozoic mass extinction.**

40

41 Current lines of evidence point to a rather rapid catastrophe ($\sim 61 \pm 48$ thousands of
42 years, ka)¹ linked to greenhouse gas emissions from the Siberian Traps large igneous
43 province (LIP)^{2,3,4}. The magmatism apparently induced a lethal combination of a
44 substantial input of relatively light carbon to the atmosphere^{4,5}, increase in global sea
45 surface temperature^{6,7,8,9,10}, sporadic to widespread anoxia^{11,12,13} or euxinia^{14,15}, and
46 ocean acidification^{16,17,18}. The exact causes and consequences, however, remain
47 controversial, and a coherent unifying scenario for the environmental evolution over
48 this important interval in Earth's history is still lacking. To reconstruct the carbon cycle
49 dynamics, we generated a new record of ocean pH for the Permian-Triassic boundary
50 (PTB) using boron isotopes (a well-established proxy for ambient seawater

51 pH)^{19,20,21,22,23} paired with carbon and oxygen isotope data. Our records are assimilated
52 into a box model, which enables us to simulate the carbon release and turnover, and
53 study its effects on the Earth's system – a critical exercise for untangling the driving
54 mechanisms of the extinction, as well as for improving our overall understanding of
55 Earth's climatic and ecological sensitivities.

56

57 **Boron isotope record of Tethys ocean acidification**

58 We generated high-resolution boron ($\delta^{11}\text{B}$), carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotope
59 records from pristine fossil brachiopod shells⁷ composed of low-magnesium calcite
60 (Fig. 1; Methods and Supplement). Our records are based on samples from three
61 stratigraphically well-characterized sections²⁴ in the Southern Alps of northern Italy –
62 Sass de Putia, Tesero and Val Brutta – where the comparatively uncondensed
63 sedimentary sequences enable a chronologically well-resolved exploration of Tethys
64 Ocean conditions at the PTB (Fig. 1a). This interval covers the global negative carbon
65 isotope excursion (CIE), a characteristic feature of the PTB, associated with major
66 biotic and environmental changes. In addition, several brachiopod specimens from a
67 distant Shangsi section in South China¹⁸ were analysed for comparison. Due to limited
68 sample availability, the Shangsi record does not overlap with that from the Southern
69 Alps; albeit a precise stratigraphic correlation at such high-resolution between the two
70 sites is rather complicated. Nevertheless, the critical decline in $\delta^{11}\text{B}$ values, as well as
71 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, following the CIE is registered by brachiopod shells from both South
72 China and Southern Alps, lending strong support to our records and that these are
73 representative of Tethys-wide conditions.

74

75 The preservation of original chemical signals in the samples and potential influences

76 from matrix contamination were thoroughly inspected using a wide suite of pre-
77 screening routines, including minor and trace element analyses (Extended Data Fig. 1;
78 Methods and Supplement). The latter showed that the composition of our samples is
79 broadly consistent with those expected for modern brachiopod species. In several
80 samples though, increased Al/Ca values were detected that are not compatible with
81 primary Al incorporation into the crystal lattice, and may be indicative of sample
82 contamination from clay sediments from the enclosing matrix. These high Al/Ca
83 values, however, did not translate into systematically enriched B/Ca or reduced $\delta^{11}\text{B}$;
84 the general trend in our $\delta^{11}\text{B}$ record can be reconstructed solely from samples with low
85 Al/Ca values (Extended Data Fig. 2). In addition, the integrity of our $\delta^{11}\text{B}$ compositions
86 was cross-checked by combining solution-based and secondary ion mass spectrometry
87 (SIMS) analyses on selected key specimens. The *in situ* nature of the SIMS approach
88 allows for direct $\delta^{11}\text{B}$ measurements within specific shell structures, providing further
89 supporting evidence that our $\delta^{11}\text{B}$ record was not significantly affected by secondary
90 impurities or post-depositional alterations.

91
92 The CIE in the Southern Alps in excess of -4.5‰ (Fig. 1c) is accompanied by a
93 decrease in $\delta^{11}\text{B}$ values of more than -1.5‰ (Fig. 1b) within some 20 ka of the latest
94 Permian (see also Extended Data Fig. 3). This is also closely reflected by a declining
95 $\delta^{18}\text{O}$ trend (Fig. 1d), suggesting a dramatic increase in seawater temperatures.
96 Following the CIE, comparably low $\delta^{11}\text{B}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are also found in South
97 China (Fig. 1). We do not observe a recovery to pre-event isotope values after the
98 boundary and into the earliest Triassic. Given the pH-dependent incorporation of $\delta^{11}\text{B}$
99 into biogenic calcite, a substantial suppression of ocean pH accompanying the CIE is
100 evident from our $\delta^{11}\text{B}$ data alone. For a quantitative estimate, we convert the $\delta^{11}\text{B}$

101 record to pH considering different $\delta^{11}\text{B}$ to pH relationships and ambient seawater $\delta^{11}\text{B}$
102 scenarios ($\delta^{11}\text{B}_{\text{sw}}$; Methods). Our preferred scenario accounts for biological ‘vital
103 effects’ on the incorporation of boron into brachiopod calcite, however, in addition we
104 also consider an alternative scenario based on aqueous borate ion relationship
105 (Extended Data Fig. 3). While the first scenario (hereinafter ‘standard case scenario’)
106 assumes that the $\delta^{11}\text{B}$ -pH dependency of brachiopod shells is influenced by their
107 internal regulating processes, the second scenario (hereinafter ‘borate ion scenario’)
108 considers boron incorporation following the inorganic $\delta^{11}\text{B}$ -pH relationship, and hence
109 the lack of vital effects. These two scenarios effectively envelop the plausible $\delta^{11}\text{B}$ -pH
110 relationships of brachiopod shells²³. Had ancient brachiopods potentially higher
111 degrees of vital effects, the $\delta^{11}\text{B}$ drop in our record would likely translate to an even
112 more extreme acidification scenario, due to the stronger internal pH regulation and
113 resulting dampened sensitivity to ambient seawater pH. The calibration choice is
114 detailed in the Methods section, and further discussion of vital effects including a pH
115 and model reconstruction considering the alternative ‘borate ion scenario’ are available
116 in the Supplement. We anchor our initial, pre-CIE $\delta^{11}\text{B}$ -derived surface ocean pH to
117 plausible pre-event conditions based on previous estimates and our model output. Our
118 $\delta^{11}\text{B}$ record then predicts the timing and the magnitude of pH fluctuation with respect
119 to the unperturbed starting conditions prior to the mass extinction event. We find, for
120 the first time, a considerable drop of ~ 0.5 units in ocean pH at the onset of the extinction
121 in the latest Permian that persists into the earliest Triassic (Fig. 2c).

122

123 **Carbon release impact on redox and nutrient feedbacks**

124 To characterise the associated carbon release and its impact on the environment, we
125 assimilate the carbon isotope and pH data into a geochemical box model (Methods; see

126 also Extended Data Figs. 4 and 5). The magnitude, dynamics, as well as the most
127 realistic time-resolved $\delta^{13}\text{C}$ composition of emitted CO_2 over the PTB is estimated by
128 fitting the model to the data. In addition to our brachiopod data, we consider numerous
129 PTB $\delta^{13}\text{C}$ bulk carbonate ($\delta^{13}\text{C}_{\text{carb}}$; Fig. 2d) as well as organic carbon isotope records
130 ($\delta^{13}\text{C}_{\text{org}}$; Fig. 2f), comprising different geographical locations and CIE magnitudes,
131 thereby assuring global representation. Our resulting degassing flux (Fig. 2a) amounts
132 to 8800×10^{12} mol CO_2 (106 Pg C, petagram = 1×10^{15} g) over the modelled duration
133 of 1 Ma (-500 ka to 500 ka relative to the CIE). A total amount of $\sim 800 \times 10^{12}$ mol CO_2
134 (9.6 Pg C) with mantle signature (-6 ‰) is initially released until -35 ka before the
135 CIE. Subsequently, the model diagnoses the emission of $\sim 8000 \times 10^{12}$ mol CO_2 (96 Pg
136 C) of isotopically substantially lighter CO_2 (-18 ‰). These low $\delta^{13}\text{C}$ values reflect the
137 metamorphic degassing of organic carbon during volcanic intrusions into coal basin
138 sediments and are required to match our pH and $\delta^{13}\text{C}$ constraints (Fig. 2b). Our outlined
139 emission scenario explains the CIE excursion without invoking light $\delta^{13}\text{C}$ signal from
140 methane clathrates. The LIP carbon budget implied by our model is also broadly
141 consistent with other independent estimates and field data^{2,3,4} (Supplement).
142 Interestingly, the emitted $\delta^{13}\text{C}$ signatures and their temporal resolution are also
143 comparable with volcanic degassing processes from the North Atlantic Igneous
144 Province during the Palaeocene-Eocene Thermal Maximum (PETM)²¹ some 56 Ma
145 ago, although the involved carbon budget for the PTB is nearly an order of magnitude
146 greater (106 Pg C as opposed to 12.2 Pg C during the PETM).

147

148 Using a new redox-resolving ocean model²⁵ we determine the ensuing series of changes
149 in the ocean chemistry (Fig. 2 and Fig. 3). We find that degassing from the Siberian
150 Traps leads to a steep increase in atmospheric pCO_2 , even though a large fraction of the

151 emitted CO₂ is dissolved in the surface ocean, transferred into depth via a gradual
152 increase in export production, and rapidly consumed and converted into bicarbonate via
153 enhanced silicate and carbonate weathering (Fig. 2). Initially, the partial pressure of
154 CO₂ in the atmosphere is relatively low in the Late Permian (~500 to ~800 ppm, *sensu*
155 *stricto* vppm; Fig. 2e). Following the CIE, at the onset of the extinction CO₂ levels rise
156 abruptly peaking at 44 ka (up to max. 4400 ppm), and remain elevated (~1500 ppm)
157 throughout the Early Triassic, consistent with previous palaeo-pCO₂
158 estimates^{5,26,27,28,29}. The sharp increase in CO₂ imposes a lasting disruption to the
159 marine carbonate cycle, prompting a severe decline in surface ocean pH (Fig. 2c),
160 which only partially recovers during the Early Triassic. In response to the carbon
161 emission, our model predicts warming by almost 10 °C (Fig. 2h) in agreement with
162 proxy-based evidence^{6,30,31}. Rates of chemical weathering strongly increase (Fig. 2g),
163 as does marine export production (Fig. 2i) and nutrient input, which is congruent with
164 the increase in detrital fluxes to the global ocean observed in numerous sedimentary
165 PTB records³².

166

167 Dissolved oxygen concentrations (Fig. 3a) in sub-surface waters decline abruptly soon
168 after the CIE and remain low over the Early Triassic due to the increase in export
169 production and respiration. The surface ocean remains oxygenated through exchange
170 with the atmosphere. Dissolved nitrate (Fig. 3b) sharply increases with the CIE,
171 promoted by a rise in sea surface temperatures (SSTs) and temperature-dependent
172 nitrogen fixation, but it declines again with a coeval increase in pelagic and benthic
173 denitrification brought on by the spread of low-oxygen conditions. Complete depletion
174 of oxygen and nitrate is only attained in the intermediate waters of the Tethys where it
175 results in an accumulation of dissolved sulphide (Fig. 2f). Under the post-PTB low-

176 oxygen conditions, ammonium (Fig. 3c), phosphate (Fig. 3d) and iron (Fig. 3e) are
177 released from seabed sediments into the overlying water column and support the rise in
178 export production and respiration in a strong positive feedback loop.

179

180 We further extend our model to simulate the turnover of stable nitrogen isotopes ($\delta^{15}\text{N}$;
181 Supplement), which reflect the composition of marine organic matter formed in the
182 surface ocean (Fig. 3h). The initial $\delta^{15}\text{N}$ decline following the CIE is linked to a rapid
183 rise in nitrogen fixation, but subsequently $\delta^{15}\text{N}$ increases due to pelagic denitrification
184 that consumes a large portion of the dissolved nitrate pool in sub-surface waters,
185 preferentially removing the light isotope (Fig. 3g). Following the consumption of the
186 excess nitrate, $\delta^{15}\text{N}$ declines again as a result of ongoing nitrogen fixation. Due to the
187 strong denitrification under low oxygen conditions, modelled plankton growth is
188 largely limited by nitrate, while nitrogen fixation is limited by phosphate. Although we
189 acknowledge that the $\delta^{15}\text{N}$ model fit, in particular close to the PTB, is less reliable due
190 to the large scatter in the data, the modelled changes explain the overall low $\delta^{15}\text{N}$ values
191 in the Early Triassic relative to the Late Permian, a feature reported from numerous
192 sedimentary records^{33,34}. This advocates for high SST and increase in the riverine
193 phosphate flux to the ocean induced by enhanced weathering and erosion as triggers of
194 the observed rise in nitrogen fixation and productivity after the PTB.

195

196 The increase in global productivity along with the depletion of dissolved oxygen
197 simulated by our redox-resolving model is consistent with data-based reconstructions.
198 Accumulation rates of organic carbon and barite determined in numerous sediment
199 cores from the Tethys and Panthalassa indicate a significant increase in export
200 production from the latest Permian into the Early Triassic^{32,35}. Marine plankton

201 communities underwent drastic restructuring over the PTB with warming and loss of
202 oxygen fostering the proliferation of prokaryotic cyanobacteria over eukaryotic algae³⁵,
203 which is consistent with the increase in nitrogen fixation predicted by the model. Global
204 loss of oxygen across the PTB has been documented by $\delta^{238}\text{U}$ and Th/U records from
205 the Tethys and Panthalassa indicating wide-spread uranium uptake in sediments after
206 the PTB^{11,12,13}. Conditions where oxygen and nitrate rather than sulphate are used as
207 terminal electron acceptors for organic matter degradation are also characteristic of
208 modern oxygen minimum zones³⁶ and lead to uranium accumulation in marine
209 sediments³⁷. Evidence for euxinic conditions, where sulphide dissolved in shallow
210 intermediate waters is transported to the euphotic zone has been reported from
211 biomarker studies¹⁵.

212

213 The carbon cycle perturbations culminate at about 100 ka after the CIE with waning
214 LIP emissions, although neither the atmospheric pCO_2 nor the marine biogeochemical
215 cycles return to pre-event conditions during the Early Triassic (Fig. 2 and Fig. 3). LIP-
216 CO_2 is converted into seawater alkalinity via enhanced chemical weathering. Upsurge
217 of export production aids the drawdown of atmospheric pCO_2 , and the ocean pH
218 recovery is additionally augmented by alkalinity production (Fig. 2k) during
219 denitrification under suboxic conditions. Neritic carbonate burial initially declines
220 following the CIE due to strong acidification of surface waters, but increases after the
221 PTB in response to an increase in alkalinity (Fig. 2j). Since calcifying phytoplankton
222 emerged only later in the Mesozoic, pelagic carbonates were absent during this time
223 and carbonate burial may have only occurred on the shelf. Under such conditions,
224 carbonate compensation would be less efficient than in the modern ocean and could
225 have led to strong calcite oversaturation of surface waters³⁸ (Fig. 2l). Our model

226 calculations are also in line with carbonate burial rates derived from strontium and
227 calcium isotope records across the PTB^{39,40}, and geologic evidence of unusually high
228 abiotic calcium carbonate precipitation in the Early Triassic⁴¹. The marine crisis,
229 however, persists through the Early Triassic, due to the delayed recovery of the redox
230 state. We note that the evolution of the surface ocean pH and the transition to suboxic
231 conditions is heavily dependent on the initial oxidation state of the ocean as shown by
232 additional model simulations and sensitivity tests (Supplement). For instance, an
233 increase or decrease of 50% in riverine phosphate input leads to substantial changes in
234 export production and nitrogen fixation, and thereby the corresponding drawdown of
235 atmospheric pCO₂. Yet these simulations fail to reproduce the proxy-based evidence,
236 such as the $\delta^{13}\text{C}$, pH or $\delta^{15}\text{N}$ records, making a strong argument in favour of the
237 ‘standard case scenario’ presented here.

238

239 **Global consequences for the marine ecosystem**

240 These findings lead us to view the PTB mass extinction as a cascading marine collapse,
241 triggered by a multi-millennial-scale voluminous injection of carbon to the atmosphere
242 by the emplacement of Siberian Traps sill intrusions^{2,42}. Its magnitude profoundly
243 altered the biogeochemical processes, setting off a chain of events that selectively
244 eliminated different groups of marine organisms⁴³. In the latest Permian, the CO₂
245 greenhouse effect resulted in strong heating and acidification of the surface ocean,
246 which prompted the initial disappearance of all reef-building taxa^{44,45}. Experiments on
247 modern organisms⁴⁶ indicate that an increase in pCO₂ alone is generally insufficient to
248 severely impair marine calcification. It is the synergic effect of acidification and rising
249 temperatures that is detrimental, and which presumably was lethal to ancient biota. The
250 subsequent extinction pulse followed in the earliest Triassic, with a strong positive

251 redox feedback driving the deoxygenation of sub-surface waters. Both our ‘standard
252 model scenario’ as well as further sensitivity tests (Supplement) suggest that the deep
253 ocean remained in a depleted oxygen state but was not seriously affected by sulphide
254 poisoning. Sulphide formation may have, however, reached toxic levels along the
255 Tethys’ continental margins and in upwelling regions of Panthalassa, where low oxygen
256 and high nutrient concentrations in ascending sub-surface waters could have promoted
257 anoxic and/or euxinic conditions, aggravating the environmental crisis. The protracted
258 recovery from suboxic conditions, nitrate limitation, possibly amplified by spreading
259 anoxia or sulphide poisoning, would have preferentially wiped out the non-motile and
260 physiologically unbuffered taxa⁴³. Together, the distinct stressors led to a physiological
261 crisis accompanied by a dramatic shrinking of the habitable realm, limiting the marine
262 refuge to a narrow zone in the upper water column^{24,47}.

263

264 Considering the vastly differing timescales and carbon budgets involved LIP carbon
265 cycle dynamics is a poor analogy for present-day fossil fuel emissions, notwithstanding
266 that, the modern geologic carbon reservoirs are insufficient for anthropogenic release
267 beyond centennial time scales. It is, however, noteworthy that even the peak emissions
268 rate during the largest known mass extinction (58×10^{12} mol CO₂ or 0.7 Pg C per year)
269 is still more than 14 times less than the current anthropogenic rate (9.9 ± 0.5 Pg C per
270 year)⁴⁸. The environmental deterioration during the PTB took several thousands of
271 years to unfold, whereas the current, unprecedented emissions rate already has started
272 to take a toll on the marine ecosystems⁴⁹. A coupled increase in atmospheric pCO₂ and
273 a decrease in surface ocean pH⁴⁹, global warming, changes in productivity as well as
274 oxygen depletion⁵⁰ have been reported world-wide, suggesting that the scenario

275 outlined here for the PTB may also be relevant for understanding future environmental
276 and climatic trends.

277 **References**

278

279 1. Burgess, S.D., Bowring, S. & Shen, S.-Z. High-precision timeline for Earth's
280 most severe extinction. *Proc. Natl. Acad. Sci.* **111**, 3316–3321 (2014).

281

282 2. Svensen, H. *et al.* Siberian gas venting and the end-Permian environmental
283 crisis. *Earth Planet. Sci. Lett.* **277**, 490–500 (2009).

284

285 3. Burgess, S.D. & Bowring, S.A. High-precision geochronology confirms
286 voluminous magmatism before, during, and after Earth's most severe extinction.
287 *Sci. Adv.* **1**, 14 (2015).

288

289 4. Saunders, A.D. Two LIPs and two Earth-system crises: the impact of the North
290 Atlantic Igneous Province and the Siberian Traps on the Earth-surface carbon
291 cycle. *Geol. Mag.* **153**, 201–222 (2016).

292

293 5. Cui, Y. & Kump, L.R. Global warming and the end-Permian extinction event:
294 Proxy and modeling perspectives. *Earth-Sci. Rev.* **149**, 5–22 (2015).

295

296 6. Sun, Y. *et al.* Lethally hot temperatures during the early Triassic greenhouse.
297 *Science* **338**, 366–370 (2012).

298

299 7. Brand, U. *et al.* The end-Permian mass extinction: A rapid volcanic CO₂ and
300 CH₄-climatic catastrophe. *Chem. Geol.* **323**, 121–144 (2012).

301

- 302 8. Winguth, A.M.E., Shields, C.A. & Winguth, C. Transition into a Hothouse
303 World at the Permian-Triassic boundary-A model study. *Palaeogeogr.*
304 *Palaeoclimatol. Palaeoecol.* **440**, 316–327 (2015).
- 305
- 306 9. Garbelli C., *et al.* Neotethys seawater chemistry and temperature at the dawn
307 of the end-Permian mass extinction. *Gondwana Res.* **35**, 272–2 (2016).
- 308
- 309 10. Wang., W. *et al.* A high-resolution Middle to Late Permian paleotemperature
310 curve reconstructed using oxygen isotopes of well-preserved brachiopod
311 shells, *Earth Planet. Sci. Lett.* **540**, 116245 (2020).
- 312
- 313 11. Lau, K.V. *et al.* Marine anoxia and delayed Earth system recovery after the end-
314 Permian extinction. *Proc. Natl. Acad. Sci.* **113**, 2360–2365 (2016).
- 315
- 316 12. Elrick, M. *et al.* Global-ocean redox variation during the middle-late Permian
317 through Early Triassic based on uranium isotope and Th/U trends of marine
318 carbonates. *Geology* **45**, 163–166 (2017).
- 319
- 320 13. Zhang, F.F. *et al.* Congruent Permian-Triassic $\delta^{238}\text{U}$ records at Panthalassic and
321 Tethyan sites: Confirmation of global-oceanic anoxia and validation of the U-
322 isotope paleoredox proxy. *Geology* **46**, 327–330 (2018).
- 323
- 324 14. Korte, C. *et al.* Carbon, sulfur, oxygen and strontium isotope records, organic
325 geochemistry and biostratigraphy across the Permian/Triassic boundary in
326 Abadeh, Iran. *Int. J. Earth Sci.* **93**, 565–581 (2004).

- 327
- 328 15. Grice, K. *et al.* Photic zone euxinia during the Permian-Triassic superanoxic
329 event. *Science* **307**, 706–709 (2005).
- 330
- 331 16. Payne, J.L. *et al.* Calcium isotope constraints on the end-Permian mass extinction.
332 *Proc. Natl. Acad. Sci.* **107**, 8543–8548 (2010).
- 333
- 334 17. Clarkson, M.O. *et al.* Ocean acidification and the Permo-Triassic mass extinction.
335 *Science* **348**, 229–232 (2015).
- 336
- 337 18. Garbelli, C., Angiolini, L. & Shen, S.-Z. Biomineralization and global change:
338 A new perspective for understanding the end-Permian extinction. *Geology* **45**,
339 19–22 (2017).
- 340
- 341 19. Hönisch, B., Hemming, N.G., Archer, D., Siddall, M. & McManus, J.F.
342 Atmospheric Carbon Dioxide Concentration Across the Mid-Pleistocene
343 Transition. *Science* **324**, 1551–1554 (2009).
- 344
- 345 20. Rae, J.W.B. *et al.* CO₂ storage and release in the deep Southern Ocean on
346 millennial to centennial timescales. *Nature* **562**, 569–573 (2018).
- 347
- 348 21. Gutjahr, M. *et al.* Very larger release of mostly volcanic carbon during the
349 Palaeocene-Eocene Thermal Maximum. *Nature* **548**, 573–577 (2017).
- 350
- 351 22. Henehan, M. *et al.* Rapid ocean acidification and protracted Earth system

- 352 recovery followed the end-Cretaceous Chicxulub impact. *Proc. Natl. Acad. Sci.*
353 **116**, 22500–22504 (2019).
- 354
- 355 23. Müller, T. *et al.* Ocean acidification during the early Toarcian extinction event:
356 Evidence from boron isotopes in brachiopods. *Geology*, *in press*
357 <https://doi.org/10.1130/G47781.1> (2020).
- 358
- 359 24. Posenato, R. Survival patterns of microbenthic marine assemblages during the
360 end-Permian mass extinction in the western Tethys (Dolomites, Italy).
361 *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **280**, 150–167 (2019).
- 362
- 363 25. Wallmann, K. *et al.* Periodic changes in the Cretaceous ocean and climate
364 caused by marine redox see-saw. *Nat. Geosci.* **12**, 456–462 (2019).
- 365
- 366 26. Retallack, G. J. A 300-million-year record of atmospheric carbon dioxide from
367 fossil plant cuticles. *Nature* **411**, 287–290 (2001).
- 368
- 369 27. Goddérès, Y. *et al.* Causal or casual link between the rise of nannoplankton
370 calcification and a tectonically-driven massive decrease in Late Triassic
371 atmospheric CO₂? *Earth Planet. Sci. Lett.* **267**, 247–255 (2008).
- 372
- 373 28. McElwain, J. C., Wagner, P. J. & Hesselbo, S. P. Fossil Plant Relative
374 Abundances Indicate Sudden Loss of Late Triassic Biodiversity in East
375 Greenland. *Science* **324**, 1554–1556, 2009.
- 376

- 377 29. Witkowski, C. R., Weijers, J. W. H., Blais, B., Schouten, S. & Damste, J. S. S.
378 Molecular fossils from phytoplankton reveal secular P_{CO2} trend over the
379 Phanerozoic. *Sci. Adv.* **4**, 7 (2018).
380
- 381 30. Joachimski, M. M. *et al.* Climate warming in the latest Permian and the
382 Permian-Triassic mass extinction. *Geology* **40**, 195–198 (2012).
383
- 384 31. Schobben, M., Joachimski, M. M., Korn, D., Leda, L. & Korte, C. Palaeotethys
385 seawater temperature rise and an intensified hydrological cycle following the
386 end-Permian mass extinction. *Gondwana Res.* **26**, 675–683 (2014).
387
- 388 32. Algeo, T.J. *et al.* Plankton and productivity during the Permian-Triassic
389 boundary crisis: An analysis of organic carbon fluxes. *Glob. Planet. Change*
390 **105**, 52–67 (2013).
391
- 392 33. Saitoh, M. *et al.* Nitrogen isotope chemostratigraphy across the Permian-
393 Triassic boundary at Chaotian, Sichuan, South China. *J. Asian Earth Sci.* **93**,
394 113–128 (2014).
395
- 396 34. Sun, Y. D. *et al.* Ammonium ocean following the end-Permian mass extinction.
397 *Earth Planet Sci. Lett.* **518**, 211–222 (2019).
398
- 399 35. Shen, J. *et al.* Marine productivity changes during the end-Permian crisis and
400 Early Triassic recovery. *Earth-Sci. Rev.* **149**, 136–162 (2015).
401

- 402 36. Canfield, D. E. Models of oxic respiration, denitrification and sulfate reduction
403 in zones of coastal upwelling. *Geochim. Cosmochim. Acta* **70**, 5753–5765
404 (2006).
405
- 406 37. Anderson, R. F. *et al.* Deep-Sea Oxygen Depletion and Ocean Carbon
407 Sequestration During the Last Ice Age. *Glob. Biogeochem. Cy.* **33**, 301–317
408 (2019).
409
- 410 38. Zeebe, R. & Westbroek, P. A simple model for the CaCO₃ saturation state of
411 the ocean: The "Strangelove", the "Neritan", and the "Cretan" Ocean. *Geochem.*
412 *Geophys. Geosy.* **4**, 1104 (2003).
413
- 414 39. Vollstaedt, H. *et al.* The Phanerozoic d^{88/86}Sr record of seawater: New
415 constraints on past changes in oceanic carbonate fluxes. *Geochim. Cosmochim.*
416 *Acta* **128**, 249–265 (2014).
417
- 418 40. Silva-Tamayo, J. C. *et al.* Global perturbation of the marine calcium cycle
419 during the Permian-Triassic transition. *Geol. Soc. Am. Bull.* **130**, 1323–1338
420 (2018).
421
- 422 41. Woods, A. Assessing Early Triassic paleoceanographic conditions via unusual
423 sedimentary fabrics and features. *Earth Sci. Rev.* **137**, 6–18 (2014).
424

- 425 42. Burgess, S.D., Muirhead, J.D. & Bowring, S.A. Initial pulse of Siberian Traps
426 sills as the trigger of the end-Permian mass extinction. *Nat. Commun.* **8**, 164
427 (2017).
428
- 429 43. Song, H.J., Wignall, P.B., Tong, J.N. & Yin, H.F. Two pulses of extinction
430 during the Permian-Triassic crisis. *Nat. Geosci.* **6**, 52–56 (2013).
431
- 432 44. Brayard, A. *et al.* Transient metazoan reefs in the aftermath of the end-Permian
433 mass extinction. *Nat. Geosci.* **4**, 693–697 (2011).
434
- 435 45. Martindale, R.C., Foster, W.J. & Velledits, F. The survival, recovery, and
436 diversification of metazoan reef ecosystems following the end-Permian mass
437 extinction event. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **513**, 100–115
438 (2019).
439
- 440 46. Reynaud, S., *et al.* Interacting effects of CO₂ partial pressure and temperature
441 on photosynthesis and calcification in a scleractinian coral. *Glob. Chang. Biol.*
442 **9**, 1660–1668 (2003).
443
- 444 47. Beatty, T.W., Zonneveld, J.-P. & Henderson, C.M. Anomalously diverse Early
445 Triassic ichnofossil assemblages in northwest Pangea: A case for shallow-
446 marine habitable zone. *Geology* **36**, 771–774 (2008).
447
- 448 48. Le Quéré, C. *et al.* Global Carbon Budget 2018. *Earth Syst. Sci. Data* **10**,
449 2141–2194 (2018).

450

451 49. Orr, J.C. *et al.* Anthropogenic ocean acidification over the twenty-first century
452 and its impact on calcifying organisms. *Nature* **437**, 681–686 (2005).

453

454 50. Schmidtko, S., Stramma, L. & Visbeck, M. Decline in global oxygen content
455 during the past five decades. *Nature* **542**, 335–339 (2017).

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457 andrews.ac.uk).

458

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473

474 **Author contributions**

475 H.J., M.G., V.L., and A.E. developed the concept and designed the study. H.J. carried
476 out chemical sample preparation as well as elemental and isotopic analyses. M.W.
477 provided isotopic micro-analyses. U.B., R.P., L.A. and C.G. provided and screened the
478 samples. R.P., L.A., C.G. and H.J. developed the age model. K.W. and S.F. devised the
479 box model and performed the analyses. H.J. wrote the manuscript, and all authors

480 discussed the results, contributed to the interpretation of the data and the final
481 manuscript.

482

483 **Competing interests**

484 The authors declare no competing interests.

485

486 **Figure 1. Brachiopod-based stable isotope data from Italy and China.** **a** Late
487 Permian palaeogeographic reconstruction (Methods) with location of the sampling
488 sites; **b** $\delta^{11}\text{B}$; **c** $\delta^{13}\text{C}$ and **d** $\delta^{18}\text{O}$ record derived from brachiopod shells from Southern
489 Alps (Sass de Putia, Tesero and Val Brutta; BWFB – Bellerophon-Werfen Formation
490 boundary) and South China (Shangsi). Error bars in **a** indicate the analytical uncertainty
491 for solution-based $\delta^{11}\text{B}$ (2SD = 0.2 ‰) and SD between multiple ion spots
492 measurements within a single shell for SIMS $\delta^{11}\text{B}$. Stratigraphy of the GSSP Meishan
493 is shown for comparison. Purple field marks the onset of the CIE as defined in our age
494 model (see Methods and Supplement), with geochronology based on latest age
495 estimates¹.

496

497 **Figure 2. Modelled marine carbonate system and climate change.** **a** CO_2 release via
498 Siberian Traps LIP degassing applied as model forcing; **b** isotopic composition of
499 released CO_2 ; **c** surface pH of Tethys Ocean; **d** carbon isotope composition of
500 carbonates deposited on Tethys shelf (data sources in Supplement); **e** global
501 atmospheric partial pressure CO_2 projected by the carbon cycle model; **f** carbon isotope
502 composition of organic carbon in sediments deposited on Panthalassa seafloor (data
503 sources in Supplement); **g** global rate of silicate (granite + basalt) and carbonate
504 weathering; **h** sea surface temperatures (SSTs) for Tethys and Panthalassa; **i** marine

505 export production of particulate organic carbon (POC) across 100 m water depth; **j**
506 burial of POC and neritic carbonate on the global shelf; **k** seawater total alkalinity (TA);
507 and **l** saturation state of surface (0–100 m) and deep waters (>1300 m) of Tethys and
508 Panthalassa with respect to calcite.

509

510 **Figure 3. Modelled redox state of the ocean, dissolved nutrient concentrations and**
511 **nitrogen cycling. a** dissolved oxygen in surface (0–100 m), intermediate (100–1300
512 m) and deep waters (>1300 m) of Tethys and Panthalassa; **b** dissolved nitrate; **c**
513 dissolved ammonium; **d** dissolved phosphate; **e** total dissolved iron; and **f** total
514 dissolved sulphide; **g** reconstruction of nitrogen cycling in Tethys Ocean; and **h**
515 nitrogen isotope composition of Tethys sediments (data sources are provided in the
516 Supplement).

517 **Methods**

518

519 **Site and sample information**

520

521 We selected fossil brachiopods from well-constrained successions of the eastern
522 Southern Alps (Sass de Putia, Tesero and Val Brutta in Italy; ref. 51 for an overview)
523 and Shangsi (China)¹⁸ spanning the Permian-Triassic boundary (PTB) interval. We
524 opted for this novel archive approach for two particular reasons; firstly because skeletal
525 components of marine calcifiers are the most appropriate boron-based pH-
526 recorders^{19,20,21,22,23} and secondly because brachiopod shells are composed of low-
527 magnesium calcite, the most robust polymorph of calcium carbonate to diagenetic
528 alterations. Our records are based on carefully chosen unaltered specimens from a
529 collection⁷ that has been extensively pre-screened involving optical and petrographic
530 inspections, scanning electron microscopy (SEM; see also in Supplement),
531 cathodoluminescence (CL), and polarising microscopy alongside criteria based on
532 trace, rare earth and redox sensitive elements to assure microstructural and chemical
533 integrity. Additionally, further related specimens from the collections of Renato
534 Posenato and Lucia Angiolini were used to complement the set, which allowed us to
535 extend the timeline and the resolution of the previous records, and capture the full span
536 of the $\delta^{13}\text{C}$ excursion. Brachiopods from these PTB sections are extremely well
537 preserved with discernible internal layers analogous to that in modern
538 brachiopods^{7,53,54,55}. The brachiopod taxa from the Southern Alps comprise the genera
539 *Comelicania*, *Comelicothyris*, *Janiceps* and *Orbicoelia* of the Class Rhynchonellata,
540 and *Ombonia* and *Orthothena* of the Class Strophomenata. To evaluate whether the
541 pH suppression observed in our record from Southern Alps was a Tethys-wide event,
542 we also included selected *Paracrurithyris* (Rhynchonellata) specimens from the distant
543 Shangsi section¹⁸ to the record for a comparison. The age model was based on a
544 stratigraphic correlation to Meishan GSSP and the latest absolute geochronologic
545 dates¹. Further description of the stratigraphy and our devised age model is available in
546 the Supplement (S1). The palaeogeographic map reconstruction including the extent of
547 the Siberian Traps province was based on geological evidence^{56,57}.

548

549 **Sample preparation and geochemical analyses**

550

551 The inner secondary layer of brachiopod shells is deemed as the most appropriate part
552 for geochemical analyses^{58,59} and was carefully sampled using a handheld precision
553 drill (Proxxon) with a mounted dental tip or a carbide pen under a binocular
554 microscope. Approximately 1–5 mg of homogenous calcium carbonate powder was
555 collected in 1.5 ml centrifuge vials. A small fraction of the powder was analysed for
556 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition on a Thermo Finnigan MAT252 stable isotope mass
557 spectrometer coupled online to an automated Kiel carbonate preparation line. The rest
558 was measured for elemental content and $\delta^{11}\text{B}$ using inductively coupled plasma mass
559 spectrometry on a Quadrupole ICP-MS (Agilent 7500x) and Thermo Scientific
560 Neptune Plus MC-ICP-MS, respectively. Measurements and sample preparation work
561 was carried out at the GEOMAR Helmholtz Centre for Ocean Research Kiel.
562 Purification and the treatment of the samples for elemental and $\delta^{11}\text{B}$ analyses was
563 carried out according to previously established protocols^{52,60}. The powder material was
564 at first thoroughly cleaned to remove any adhering clays, then oxidatively cleaned using
565 buffered peroxide and finally dissolved in 0.5 M HNO_3 . Prior to $\delta^{11}\text{B}$ analyses, samples

566 were additionally screened for chemical consistency by checking various elemental
567 ratios (Al/Ca, B/Ca, Mg/Ca, Sr/Ca, Mn/Ca, Fe/Ca and U/Ca; Extended Data Fig. 1; see
568 also Supplement S2). Although few samples had elevated Al/Ca, similar to
569 observations from previous studies²¹, this did not translate into altered $\delta^{11}\text{B}$ values, as
570 supported by the good agreement between solution-based and *in situ* SIMS
571 measurements. Likewise, we observed variable B/Ca, Mg/Ca, Sr/Ca, Mn/Ca, Fe/Ca and
572 U/Ca, however, with the exception of few samples, measured values were within the
573 range of recent brachiopods⁵⁸ and without significant systematic effect on the $\delta^{11}\text{B}$
574 values. We also underscore that, for most parts, our record is based on several
575 specimens per stratigraphic horizon, with good agreement in $\delta^{11}\text{B}$ values between them
576 despite variable Al/Ca or other ratios, implying that any potential source of
577 contamination to the samples had limited impact on the $\delta^{11}\text{B}$ values. This is also
578 supported by the very depleted B/Ca, but elevated and variable Al/Ca of the enclosing
579 matrix based on three samples of Late Permian cement (Extended Data Fig. 1), which
580 was the likely source. Ultimately though, as mentioned in the main text, our overall
581 $\delta^{11}\text{B}$ trends may still be reconstructed when samples with low Al/Ca only are taken into
582 account. Our total procedural blanks were below <100 pg B ($\delta^{11}\text{B} \sim -0$ – 20 ‰) and hence
583 negligible considering the typical sample size of 10–50 ng B. The external
584 reproducibility on $\delta^{11}\text{B}$ was ± 0.2 ‰ (2SD) assessed by repeated measurements of
585 purified carbonate standard reference materials measured along with samples and
586 treated identically ($\delta^{11}\text{B} = 24.51 \pm 0.18$ ‰, $n = 5$ for the coral reference material JCp-
587 1; and $\delta^{11}\text{B} = 15.96 \pm 0.21$ ‰, $n = 16$ for our in-house brachiopod standard MVS-1), in
588 line with our previously published results⁵². In addition, *in situ* boron isotope
589 measurements were carried out on selected key specimens using secondary ion mass
590 spectrometry (SIMS). This approach allows for determination of $\delta^{11}\text{B}$ values in
591 brachiopod shells directly, without the chemical processing of samples, and with
592 measured isotopic ratios being directly comparable to the solution-based MC-ICP-MS
593 technique^{52,61}. SIMS analyses and sample preparation was done at the GFZ German
594 Research Centre for Geosciences – Helmholtz Centre Potsdam. Measurements were
595 performed on a CAMECA 1280-HR SIMS instrument as described in detail in
596 Supplement (S3). In brief, cross-sections of brachiopod shells were embedded in epoxy,
597 polished and coated with gold. We used a $^{16}\text{O}^-$ primary beam operated in Köhler
598 illumination with intensity varying between approximately 40 to 60 nA that was
599 focused into an aperture delimited spot of ~ 30 μm . The analyses were conducted in a
600 multi-collection mode by simultaneously measuring ^{10}B and ^{11}B on electron
601 multipliers. For instrument calibration and reporting of measured isotopic ratios to the
602 common NIST 951 scale we used the inorganic calcite standard reference material
603 UWC-1⁶². The count rate on the $^{11}\text{B}^+$ mass station on the UWC-1 was typically in the
604 range 5000 to 10,000 ions/second, which translated to an uncertainty ~ 1 to 1.5 ‰ (SD)
605 for individual analyses (for the brachiopod samples the count rate was usually at least
606 double that of the UWC-1). The external analytical repeatability based on 82
607 determinations on the UWC-1 over 4 days of the measurement session was better than
608 ± 1.4 ‰ (SD, $n = 82$). Results are shown as a mean of multiple ion spot measurements
609 within a single specimen with SD between them.

610

611 pH calculation

612

613 A prerequisite for the reconstruction of pH from $\delta^{11}\text{B}$ values of marine biogenic
614 carbonates is the knowledge of $\delta^{11}\text{B}$ composition of seawater ($\delta^{11}\text{B}_{\text{sw}}$). Boron in
615 seawater is homogenous with a residence time of approximately 11 to 20 Ma, and thus

616 the $\delta^{11}\text{B}_{\text{sw}}$ needs to be constrained for the PTB. The $\delta^{11}\text{B}_{\text{sw}}$ composition of the modern
617 ocean is 39.6 ‰, but was proposed to have been lower in the past (~37 ‰ 60 Ma ago)⁶³.
618 Permian $\delta^{11}\text{B}_{\text{sw}}$ values were previously calculated by modelling of the boron
619 geochemical cycle suggesting $\delta^{11}\text{B}_{\text{sw}}$ of ~38 ‰ for the Early Permian (Late Sakmarian)
620 and $\delta^{11}\text{B}_{\text{sw}}$ of ~34‰ for the latest Permian, just prior to the PTB⁶⁵. To provide a further
621 constrain on the $\delta^{11}\text{B}_{\text{sw}}$, but not obviating previous estimates, we considered a range of
622 values that effectively envelopes the possible $\delta^{11}\text{B}_{\text{sw}}$, yet allows for the full expression
623 of the proxy. Assuming that boron is incorporated into brachiopod calcite following the
624 inorganic borate ion fractionation⁶⁵ with negligible vital effects, the maximum integer
625 $\delta^{11}\text{B}_{\text{sw}}$ that enables the calculation of pH from all our brachiopod $\delta^{11}\text{B}$ values within
626 the dynamic range of the proxy is 38 ‰, with values ≥ 39 ‰ being beyond the sensitivity
627 of the proxy at the lower pH spectrum. On the other hand, applying a brachiopod
628 calibration that accounts for biological influence on the incorporation of boron⁶⁶, the
629 highest feasible integer $\delta^{11}\text{B}_{\text{sw}}$ is 35 ‰ (similarly, values ≥ 36 ‰ are beyond the proxy
630 range at the lower pH spectrum). A lower-end limit on the $\delta^{11}\text{B}_{\text{sw}}$ can be placed by tying
631 our average pre-event brachiopod $\delta^{11}\text{B}$ (14 ± 0.5 ‰, 2SD, $n = 7$; based on the mean
632 composition of brachiopods from beds wPK5 top, wPK6A, and wPK6A base; note that
633 the specimens from beds PK4 are not included due less reliable constrains on their age;
634 see also Supplement S1) to a probable pre-event pH conditions and inversely derive the
635 $\delta^{11}\text{B}_{\text{sw}}$. Considering that modern ocean mean pH is 8.1, and Late Permian was a high
636 pCO₂ world, but the ocean did not contain a carbonate buffer due to the lack of pelagic
637 carbonate producers, it is reasonable to assume that pre-event pH must have been lower
638 than today. Assuming a mean pre-event pH of ~7.8, based on model-derived constraints
639 of Late Permian pH for a ‘Neritan’ ocean⁶⁷, the $\delta^{11}\text{B}_{\text{sw}}$ of ~38 ‰ and ~35 ‰ via borate
640 ion fractionation and brachiopod calibration, respectively, may be calculated (in this
641 case higher pre-event pH values would result in lower $\delta^{11}\text{B}_{\text{sw}}$ estimates). The choice of
642 the pre-event pH value, and hence $\delta^{11}\text{B}_{\text{sw}}$, can be further supported by additional runs
643 of our geochemical box model when forced not to violate constrains given by LIP
644 degassing and the global $\delta^{13}\text{C}$ record (see Supplement S4).

645
646 In addition to the $\delta^{11}\text{B}_{\text{sw}}$, the application of an appropriate archive-specific $\delta^{11}\text{B}$
647 calibration is required in order to calculate pH from $\delta^{11}\text{B}$ values. Typically, more recent
648 reconstructions spanning the Neogene employ extant archives (e.g. foraminifera or
649 corals) for which a pH-dependent $\delta^{11}\text{B}$ calibration can be made using culture or field
650 studies in order to assess the role of vital effects due to their internal biological
651 processes. This is, however, not possible for any Palaeozoic brachiopods which are
652 extinct and thus such assessments must be made indirectly. Similar to the calculation
653 of $\delta^{11}\text{B}_{\text{sw}}$, in order to account for different influences on the incorporation of boron into
654 brachiopod shells we consider two different calibrations; the inorganic $\delta^{11}\text{B}$ -to-pH
655 relationship of aqueous borate ion⁶⁵ and a brachiopod calibration bracketing their vital
656 effects⁶⁶. Because vital effects, as in other calcifiers, are also undoubtedly inherent to
657 brachiopods, we chose the pH reconstruction based on brachiopod calibration⁶⁶ as our
658 preferred scenario (‘standard case scenario’). However, for comparison we also provide
659 a second detailed scenario based on pH values calculated using the borate ion
660 relationship (‘borate ion scenario’; Extended Data Fig. 3; and detailed in Supplement
661 S4).

662
663 Two further calibrations can be found in the literature; a calibration based on modern
664 terebratellids⁶⁸ and a calibration based on cultured *Magellania venosa*⁵². The first one⁶⁸
665 results in pH estimates rather similar to that of the brachiopod calibration of ref. 66. In

666 comparison, the *M. venosa* calibration⁵² results being highly sensitive within the
667 defined $\delta^{11}\text{B}_{\text{sw}}$ envelope, with only minor $\delta^{11}\text{B}$ variations resulting in extreme pH
668 change, which are in most instances beyond the dynamic proxy range. A pH
669 reconstruction is, nonetheless, feasible using the *M. venosa* calibration⁵² if $\delta^{11}\text{B}_{\text{sw}} < 30$
670 ‰. Such low $\delta^{11}\text{B}_{\text{sw}}$ values, however, at present appear rather unlikely for the PTB.
671 Hence, while the *M. venosa* calibration appears to be applicable to other recent cold-
672 water species as well, we suspect that it is not suited for Palaeozoic brachiopods.
673 Moreover, many modern terebratellids, and specifically *M. venosa*, thrive in highly
674 dynamic cold-water regimes characteristic of large seasonal variations and as a result
675 likely exhibit stronger vital effects than ancient warm-water dwelling species.

676
677 Species-specific vital effects may further complicate the use of one general
678 calibration⁶⁸. To overcome this, and because the use of multiple brachiopod species
679 appears inevitable for providing a PTB record of sufficient temporal resolution, we
680 considered the following measures. First, we strictly limited the number of species used
681 in our record, but in particular brachiopod classes since brachiopods vary mostly at a
682 higher taxonomic level⁶⁹. Second, because vital effects are closely linked to organism's
683 niche, we examined the habitat and morphology parallels between the species used.
684 Finally, we devised the record taking into account stratigraphic overlap between the
685 different species during the pre-event as well as the event conditions, giving us
686 confidence that the final reconstruction is not significantly affected by species-specific
687 offsets. Indeed, the overall $\delta^{11}\text{B}$ trend of our full record holds when solely based on one
688 brachiopod group (Rhynchonellata) from one site (Dolomites, N. Italy; Extended Data
689 Fig. 2).

690
691 The Late Permian record prior to the CIE is almost exclusively based on *Comelicania*
692 sp., but also includes two specimens of *Janiceps* sp. (both Rhynchonellata), which show
693 a close agreement, not larger than typical intraspecific variations among different
694 *Comelicania* sp. shells. Just after the CIE, the record still includes several *Comelicania*
695 sp., but also few other species belonging to both Rhynchonellata and Strophomenata.
696 Note that bed wPK11B (app. 7 ka relative to the CIE) comprises *Janiceps* sp. and
697 *Comelicothyris* sp. (both Rhynchonellata) as well as *Ombonia* sp. (Strophomenata)
698 specimens, which show highly similar $\delta^{11}\text{B}$ values (13.18 ± 0.48 , SD between
699 specimens, $n = 6$), further supporting the fact that interspecific variations, even at a
700 class level, are minimal and do not significantly impact our $\delta^{11}\text{B}$ values. The latest part
701 of our record documenting acidification, despite the scarcity of brachiopods in these
702 beds, is based on both brachiopod classes with multiple specimens of *Orbicoelia* sp.
703 (Rhynchonellata) and *Teserina* sp. (Strophomenata) from northern Italy, as well as
704 *Paracrurithyris* sp. (Rhynchonellata) from South China, offering firm evidence for the
705 pH trends presented in this study.

706
707 The effect of the dissociation constant for boric acid (pK_{B}^*) on the calculated pH is
708 comparatively only very minor. For our pH calculation we used $\text{pK}_{\text{B}}^* = 8.60$,
709 corresponding to the typical pre-event temperatures of about 25 °C and salinity of 35,
710 based on our data as well as conodont-derived pre-event temperatures^{6,30} and
711 considering that the general Late Permian salinity^{31,70} and major ion chemistry and
712 mineralogy⁷⁰ was largely similar to present day conditions. We note that a temperature
713 increase by 5 or 10 °C for example, would give a pK_{B}^* of 8.54 or 8.48, which would
714 translate to a decrease in pH values by 0.06 and 0.12 units, respectively. This would
715 only magnify the reported pH decline simultaneous with the major phase of warming,

716 although at such low pH range the pK_B^* influences on pH values would be largely
717 within the uncertainties.

718

719 **Model setup**

720

721 A geochemical box model was set up to simulate the processes in the global ocean
722 based on a recent ocean circulation model⁸ for the PTB (see Supplement S4 for a
723 detailed description of the model). Basin volumes, seafloor areas, and the water fluxes
724 between the boxes employed in the model are taken from the circulation model
725 (Extended Data Fig. 5). The recently developed redox-resolving biogeochemistry
726 model REDBIO²⁵ was coupled to the box model to simulate the biogeochemical
727 turnover in the ocean. REDBIO considers the following dissolved tracers: oxygen,
728 nitrate, ammonium, phosphate, ferric iron, ferrous iron, total dissolved sulphide,
729 dissolved inorganic carbon (¹²C and ¹³C) and total alkalinity. All tracer inventories
730 change over time due to weathering inputs from land, CO₂ and O₂ fluxes across the
731 ocean–atmosphere interface, nitrogen fixation, denitrification and redox-dependent
732 fluxes at the seabed. Continental weathering and degassing fluxes, surface temperatures
733 and atmospheric pCO₂ were simulated using the GEOCARB process formulations^{72,73},
734 whereas marine $\delta^{13}\text{C}$ values were calculated as described in a previous box model⁷⁴.
735 REDBIO was further extended to simulate the turnover of stable nitrogen isotopes in
736 the ocean, considering total concentrations of dissolved nitrate and ammonium as well
737 as the concentrations of ¹⁵N-nitrate and ¹⁵N-ammonium.

738

739 The model was run for a period of 2 Ma to reach a Late Permian equilibrium.
740 Subsequently, a pulse of volcanic/metamorphic CO₂ was released to study the
741 consequences of LIP degassing. The boundary parameters including the equilibrium
742 climate sensitivity of 3 °C per doubling of pCO₂ were chosen based on the
743 GEOCARB⁷⁵ models. Model results are shown on a timescale where the zero point is
744 set at the onset of the negative carbon isotope excursion (CIE). The CO₂ flux induced
745 by LIP degassing and its isotopic composition were varied systematically until the $\delta^{13}\text{C}$
746 of carbonates deposited on the continental shelf of the Tethys (see Supplement S4 for
747 data sources) and the pH values in Tethys surface water were consistent with the
748 available data (Fig. 2). Comparison of our model-derived atmospheric pCO₂ with
749 previously published estimates⁵ based on stomatal indices is available in Supplement
750 (S5). Throughout the manuscript we use the terminology Tethys Ocean, which
751 combines both Neotethys and Palaeotethys Oceans, since they are represented by a
752 common box in the model.

753 **Supplementary Information** is available accompanying this contribution with further
754 details on the stratigraphy and age model (S1), brachiopod samples (S2), analytical
755 methods (S3), modelling (S4), and a comparison with stomatal pCO₂ estimates (S5).

756

757 **Data availability**

758 We have chosen not to deposit the data in a repository at this time but all geochemical
759 data analysed during this study are accessible in the **Supplementary Data** file.

760

761 **Code availability**

762 Computer code is available upon reasonable request from K.W.
763 (kwallmann@geomar.de).

764

765 **References (only in Methods)**

766

767 51. Posenato, R. Marine biotic events in the Lopingian succession and latest
768 Permian extinction in the Southern Alps (Italy). *Geol. J.* **45**, 195–215 (2010).

769

770 52. Jurikova, H. *et al.* Boron isotope systematics of cultured brachiopods: response
771 to acidification, vital effects and implications for palaeo-pH reconstruction.
772 *Geochim. Cosmochim. Acta* **248**, 370–386 (2019a).

773

774 53. Broglio Loriga, C., Neri C., Pasini, M. & Posenato, R. Marine fossil
775 assemblages from Upper Permian to lowermost Triassic in the western
776 Dolomites (Italy). In: Cassinis, G. (Ed.) Permian and Permian–Triassic
777 boundary in the South-Alpine segment of the western Tethys, and additional
778 reports. *Memorie della Societa Geologica Italiana* **34**, 5–44 (1988).

779

780 54. Posenato, R. The athyridoids of the transitional beds between Bellerophon and
781 Werfen formations (uppermost Permian, Southern Alps, Italy). *Riv. Ital.*
782 *Paleontol. S.* **1071**, 197–226 (2001).

783

784 55. Kearsey, T., Twichett, R.J., Price, G.D. & Grimes, S.T. Isotope excursion and
785 palaeotemperature estimates from the Permian/Triassic boundary in the
786 Southern Alps (Italy). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **279**, 29–40
787 (2009).

788

789 56. Muttoni, G. *et al.* Opening of the Neo-Tethys Ocean and the Pangea B to Pangea
790 A transformation during the Permian. *GeoArabia* **14**, 17–48.

791

792 57. Reichow, M.K. *et al.* The timing and extent of the eruption of the Siberian Traps
793 large igneous province: Implications for the end-Permian environmental crisis.
794 *Earth Planet. Sci. Lett.* **277**, 9–20 (2009).

795

796 58. Brand, U., Logan, A., Hiller N. & Richardson J. Geochemistry of modern
797 brachiopods: applications and implications for oceanography and
798 paleoceanography. *Chem. Geol.* **198**, 305–334 (2003).

799

800 59. Rollion-Bard, C. *et al.* Assessing the biomineralisation processes in the shell
801 layers of modern brachiopods from oxygen isotopic composition and elemental
802 ratios: Implications for their use as paleoenvironmental proxies. *Chem. Geol.*

- 803 **524**, 49–66 (2019).
804
- 805 60. Jurikova, H., *et al.* Incorporation of minor and trace elements into cultured
806 brachiopods: Implications for proxy application with new insights from a
807 biomineralisation model. *Geochim. Cosmochim. Acta* **286**, 418–440 (2020).
808
- 809 61. Jurikova, H. *et al.* Boron isotope composition of the cold-water coral *Lophelia*
810 *pertusa* along the Norwegian margin: Zooming into a potential pH-proxy by
811 combining bulk and high-resolution approaches. *Chem. Geol.* **513**, 143–152
812 (2019b).
813
- 814 62. Kasemann, S.A., S.A., Schmidt, D.N., Bijima, J. & Foster, G.L. *In situ* boron
815 isotope analyses in marine carbonates and its application for foraminifera and
816 palaeo-pH. *Chem. Geol.* **260**, 138–147 (2009).
817
- 818 63. Lemarchand, D., Gaillardet, J., Lewin, É. & Allègre, C. J. The influence of
819 rivers on marine boron isotopes and implications for reconstructing past ocean
820 pH. *Nature* **408**, 951–954 (2000).
821
- 822 64. Joachimski, M.M., Simon, L., van Geldern, R. & Lécuyer, C. Boron isotope
823 geochemistry of Paleozoic brachiopod calcite: Implications for a secular change
824 in the boron isotope geochemistry of seawater over the Phanerozoic. *Geochim.*
825 *Cosmochim. Acta* **69**, 4035–4044 (2005)
826
- 827 65. Klochko, K., Kaufman, A.J., Wengsheng, Y., Byrne, R.H. & Tossell, J.A.
828 Experimental measurement of boron isotope fractionation in seawater. *Earth*
829 *Planet. Sci. Lett.* **248**, 276–285 (2006).
830
- 831 66. Lécuyer, C., Grandjean, P., Reynard, B., Albarède, F. & Telouk, P. ¹¹B/¹⁰B
832 analysis of geological materials by ICP-MS Plasma 54: application to the boron
833 fractionation between brachiopod calcite and seawater. *Chem. Geol.* **186**, 45–
834 55 (2002).
835
- 836 67. Ridgwell, A. A Mid Mesozoic Revolution in the regulation of ocean chemistry.
837 *Mar. Chem.* **217**, 339–357 (2005)
838
- 839 68. Penman, D.E., Hönisch, B., Rasbury, E.T., Hemming, N.G., & Spero, H.J.
840 Boron, carbon, and oxygen isotopic composition of brachiopod shells: Intra-
841 shell variability, controls, and potential as a paleo-pH recorder. *Chem. Geol.*
842 **340**, 32–39 (2013).
843
- 844 69. Garbelli, C., Angiolini, L., Brand, U. & Jadoul, F. Brachiopod fabric, classes
845 and biogeochemistry: implications for the reconstruction and interpretation of
846 seawater carbon-isotope curves and records. *Chem. Geol.* **371**, 60–67 (2014).
847
- 848 70. Khiel, J.T. & Shields, C.A. Climate simulations of the latest Permian:
849 Implications for mass extinction. *Geology* **33**, 757–760 (2005).
850

- 851 71. Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A. & Demicco,
852 R.V. Oscillations in Phanerozoic Seawater Chemistry: Evidence from Fluid
853 Inclusions. *Science* **294**, 1086–1088 (2001).
854
- 855 72. Berner, R.A. & Kothavala, Z. GEOCARB III: A revised model of atmospheric
856 CO₂ over Phanerozoic time. *Am. J. Sci.* **301**, 182–204 (2001).
857
- 858 73. Royer, D.L., Donnadieu, Y., Park, J., Kowalczyk, J. & Godderis, Y. Error
859 analysis of CO₂ and O₂ estimates from the long-term geochemical model
860 GEOCARBSULF. *Am. J. Sci.* **314**, 1259–1283 (2014).
861
- 862 74. Wallmann, K., Schneider, B. & Sarnthein, M. Effects of eustatic sea-level
863 change, ocean dynamics, and nutrient utilization on atmospheric pCO₂ and
864 seawater composition over the last 130,000 years. *Clim. Past.* **12**, 339–375
865 (2016).
866
- 867 75. Berner, R.A. GEOCARB II: A revised model of atmospheric CO₂ over
868 Phanerozoic time. *Am. J. Sci.* **294**, 56–91 (1994).















