Decoupled $\delta^{11}B$ and $\delta^{13}C$ during the Late Permian: Implications for carbon cycle perturbations during the mass extinction event

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The Permian-Triassic boundary (PTB) witnessed the most severe environmental and biotic crisis identified in the Earth's geological record. Current lines of evidence on causation point towards massive flood-basalt volcanism from Siberian traps, involving a combination of global warming by ~6°C, substantial input of relatively light carbon to the atmosphere, sporadic anoxia or euxinia, and ocean acidification. In order to reconstruct potential changes in seawater chemistry during this time interval, we examined the boron isotope composition ($\delta^{11}B$) of pristine brachiopod shells. Although to date hardly applied in Paleozoic settings such as the PTB [1], the $\delta^{11}B$ of marine calcium carbonate is considered to be one of the most reliable paleo-pH proxies [e.g. 2], providing the archive is free from post-depositional diagenetic alterations. Using selected $\delta^{11}B$ to pH relationships and bulk seawater $\delta^{11}B$ scenarios, we present a high-resolution seawater pH record for the Western Tethys covering ~10 ky [3] during the latest phase of the Permian extinction [4]. This interval recorded a negative $\delta^{13}C$ excursion (CIE) in excess of ~4 ‰ preceding the extinction event by a few millennia [5]. Our $\delta^{11}B$ results show a maximum variation between 12.9 and 14.3 ‰ throughout the record, yet suggesting none to minor pH change during the CIE. Given the very good preservation of our specimens, this finding may argue against pronounced ocean acidification or point to pH buffering mechanisms associated with CIE. Combined with a quantitative modelling approach we delineate potential atmospheric and oceanic conditions and changes in the carbon budget involved.

[1] Clarkson et al. (2015) *Science* **348**, 229-232. [2] Foster (2008) *EPSL* **271**, 254-266. [3] Posenato (2010) *Geol. J.* **45**, 195-215. [4] Song et al. (2012) *Nat. Geosci.* **6**, 52-56. [5] Brand et al. (2012) *Chem. Geol.* **323**, 121-144.