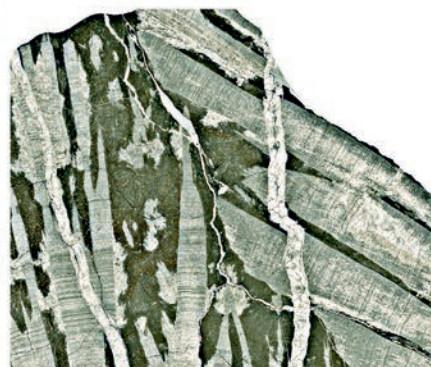
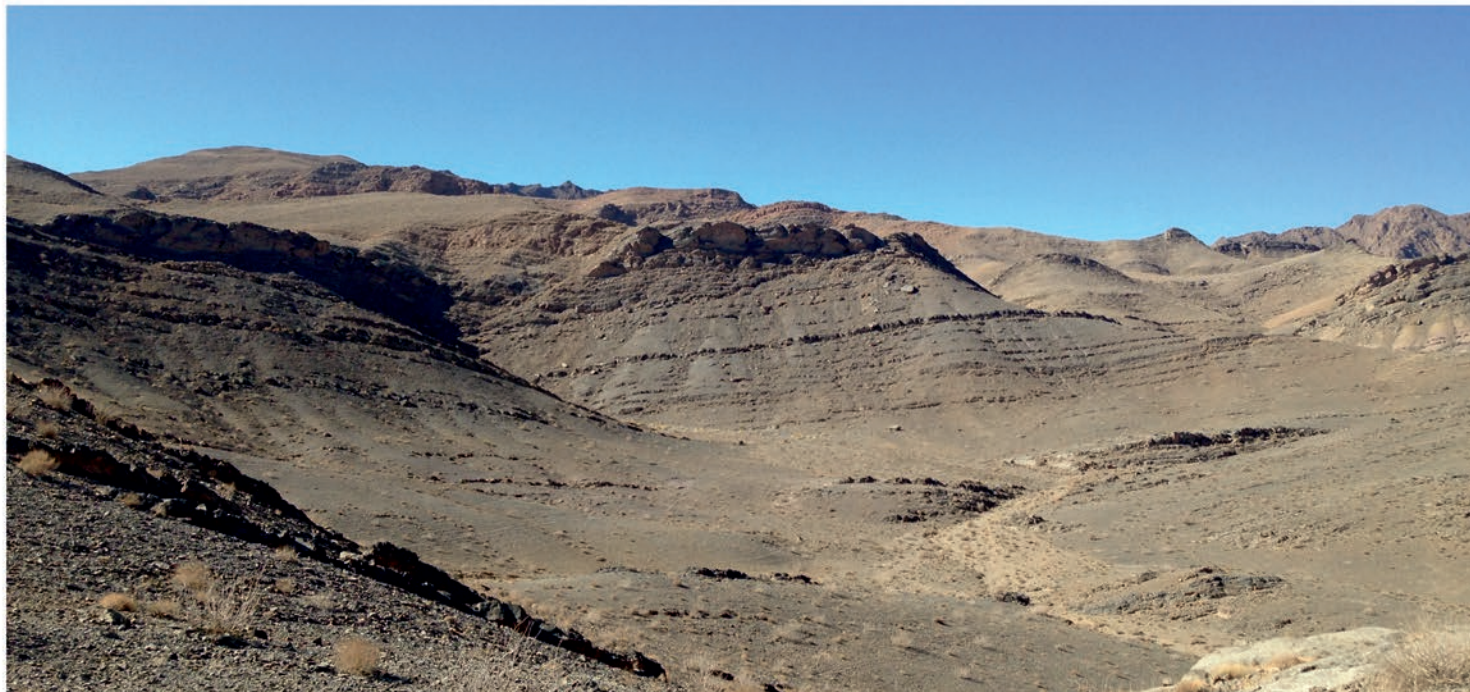




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Assessing ocean acidification and carbon cycle perturbations during the end-Permian extinction using boron isotopes

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The Permian-Triassic mass extinction represents the most severe environmental crisis in Earth's history, which dictated the course for evolution of life until today. Volcanism from Siberian traps played a significant role involving a substantial input of relatively light carbon into the atmosphere leading to a combination of global warming by ~6°C, sporadic anoxia or euxinia, and ocean acidification. However, its detailed manifestation and environmental impact is yet to be fully understood. This lack of knowledge also extends to a better quantification of emitted and sequestered carbon budgets (cf. Gutjahr et al., 2017).

In order to reconstruct potential changes in seawater chemistry during this time interval, we examined the boron isotope composition ($\delta^{11}\text{B}$) of brachiopod shells. Although rarely applied to Paleozoic settings such as the Permian-Triassic (Clarkson et al., 2015), the $\delta^{11}\text{B}$ of marine calcium carbonate is considered one of the most reliable paleo-pH proxies (e.g., Foster, 2008; Hönisch et al., 2012). The principle of the $\delta^{11}\text{B}$ proxy is based on the speciation of boron in seawater, where it is present as boric acid $[\text{B}(\text{OH})_3]$ and borate ion $[\text{B}(\text{OH})_4^-]$, and their relative proportion is pH dependant. Furthermore, because an isotopic fractionation exists between the two species, and principally borate ion is incorporated into the crystal lattice, the $\delta^{11}\text{B}$ composition of biogenic calcium carbonate can be used to reconstruct ancient seawater pH.

Brachiopods present a rich, and largely underutilised archive for Phanerozoic reconstructions considering their high abundance in the geological record that can be traced back to the early Cambrian. Moreover, their shell made of low-magnesium calcite

makes these marine calcifiers more resilient to post-depositional diagenetic alterations of primary chemical signals. We performed $\delta^{11}\text{B}$ analyses (together with B/Ca and other major and trace element-to-Ca ratios as additional controls on preservation and environmental conditions) on carefully chosen pristine specimens (class Rhynchonellata and Strophomenata) from Val Brutta, Sass de Putia and Tesero sections in northern Italy. These sections cover the negative $\delta^{13}\text{C}$ excursion in excess of 4‰ (Brand et al., 2012) and are associated with major climate and environmental perturbations that led to the mass extinction event. Using selected $\delta^{11}\text{B}$ to pH relationships and bulk seawater $\delta^{11}\text{B}$ scenarios we reconstructed a high-resolution seawater pH record for the Paleo-Tethys Ocean. Our $\delta^{11}\text{B}$ results show a significant decline in $\delta^{11}\text{B}$ succeeding the $\delta^{13}\text{C}$ excursion, suggesting a substantial drop in seawater pH at the onset of the extinction event in the Late Permian related to carbon cycle perturbations. To corroborate the extent of ocean acidification, we additionally measured several brachiopod specimens from the Shangsi section, South China (Garbelli et al., 2017). This confirms our findings from Italy, and implies that ocean acidification may have been a widespread phenomenon in the Paleo-Tethys, adversely impacting the marine life. Combining our pH record paired with $\delta^{13}\text{C}$ data with a quantitative modelling approach we aim to delineate the unfolding carbon cycle dynamics and budget involved that may have been responsible for initiating the catastrophic extinction.

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