

## Abstract

CO<sub>2</sub>-induced ocean acidification and associated decrease of seawater carbonate saturation state contributed to multiple environmental crises in Earth's history and currently poses a major threat for marine calcifying organisms. Owing to their high abundance and good preservation in the Phanerozoic geological record, brachiopods present an expedient taxon of marine calcifiers for palaeo-proxy applications as well as studies on biological mechanism to cope with environmental change. The boron isotope composition of marine calcifiers is regarded as one of the most reliable palaeo-pH proxies, yet until now hardly applied to brachiopods.

To investigate the geochemical and physiological responses of brachiopods to prolonged low-pH conditions we cultured *Magellania venosa*, *Terebratella dorsata* and *Pajaudina atlantica* under controlled experimental settings over a period of two years. Our experiments demonstrate that brachiopods form their calcite shells under strong biological control, which enables them to survive and grow under low-pH conditions and even in seawater strongly undersaturated with respect to calcite (pH = 7.35,  $\Omega_{\text{cal}} = 0.6$ ). Using boron isotope ( $\delta^{11}\text{B}$ ) systematics including MC-ICP-MS as well as SIMS analyses, validated against *in vivo* microelectrode measurements, we show that this resilience is achieved by strict regulation of the calcifying fluid pH between the epithelial mantle and the shell. We provide a culture-based  $\delta^{11}\text{B}$ -pH calibration, which as a result of the internal pH regulatory mechanisms deviates from the inorganic borate ion to pH relationship, but confirms a clear yet subtle pH dependency for brachiopods. At a micro-scale level, the incorporation of  $\delta^{11}\text{B}$  appears to be principally driven by a physiological gradient across the shell, where the  $\delta^{11}\text{B}$  of the innermost calcite records the internal calcifying fluid pH while the composition of the outermost layers is also influenced by seawater pH. This study details for the first time the functioning of the boron isotope proxy in brachiopods and lays the ground for its application in palaeo-reconstructions (Chapter 3).

The Permian-Triassic boundary (PTB) marked the most severe environmental crisis identified in the geological record that occurred about 252 million years ago (Ma) and dictated the course for evolution of life onwards. While magmatism from Siberian Traps certainly played a significant role, the causal trigger and its feedbacks are yet to be fully understood. Deciphering the carbon budgets involved and the environmental responses is key for understanding the functioning of Earth's climate system and for improving our future

predictions. We present a new boron isotope-derived seawater pH record that demonstrates a substantial and lasting suppression of seawater pH at the onset of the extinction in the latest Permian. Combined with carbon and oxygen isotope data, our results are integrated in a geochemical model that resolves the carbon cycle dynamics as well as ocean redox conditions. We find that the initial ocean acidification was intimately linked to a large pulse of carbon degassing from the Siberian sill intrusions. We unravel the consequences of the greenhouse effect on the marine environment, and show how a positive feedback rooted in redox-dependent nutrient turnover gave rise to widespread de-oxygenation and sulphide poisoning of the oceans in the earliest Triassic. Our findings enable us to assemble the first consistent biogeochemical reconstruction of key processes resulting in the largest Phanerozoic mass extinction (Chapter 4).

Apart from boron isotopes, B/Ca ratio and other element/Ca ratios have been suggested as promising proxies for carbonate system parameters. Yet to date these proxies have not been examined in cultured brachiopods and only little is known on the mechanisms that control the incorporation of various key elements into brachiopod calcite. We use our cultured brachiopods (*M. venosa* and *P. atlantica*) to evaluate the feasibility and robustness of multiple element/Ca ratios as proxies in brachiopods, specifically Li/Ca, B/Ca, Na/Ca Mg/Ca, Sr/Ca and Ba/Ca. The experimental setup used for this study comprised two control aquariums ( $\text{pH}_0 = 8.0$  and  $8.15$ ,  $T = 10$  °C) and treatments where pH ( $\text{pH}_1 = 7.6$  and  $\text{pH}_2 = 7.35$ ), temperature ( $T = 16$  °C) and Mg/Ca composition of the seawater were manipulated. Our results indicate the following dependencies for *M. venosa*: Li/Ca correlates with pH, or alternatively  $\Omega_{\text{cal}}$ ; Mg/Ca varies as a function of TA or temperature and TA; and Sr/Ca correlates with DIC. For B/Ca no trend with pH was found, but we observed a weak link to TA. Ba/Ca or Na/Ca did not show any relationship with carbonate system parameters. In addition, computed tomography analyses of shells grown under the different experimental treatments were carried out. We quantified calcite/punctae ratios, which indicate that shells build under environmental stress, including acidification, but in particular increased temperature contain relatively more pore space than shells grown under control or natural conditions. These findings have implications for the use of calcite/punctae ratios as a novel proxy (Chapter 5).