Geophysical Research Abstracts
Vol. 20, EGU2018-8970, 2018
EGU General Assembly 2018

Incorporation of boron isotopes into brachiopod shell calcite: implications for paleo-pH reconstructions

Hana Jurikova (1), Volker Liebetrau (1), Marcus Gutjahr (1), Claire Rollion-Bard (2), Marian Y. Hu (3), Daniela Henkel (1), Claas Hiebenthal (1), Stefan Krause (1), Mark Schmidt (1), Jürgen Laudien (4), and Anton Eisenhauer (1)

(1) GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel, Germany (hjurikova@geomar.de), (2) Institut de Physique du Globe de Paris, France, (3) Physiologisches Institut, Christian-Albrechts-Universität zu Kiel, Germany, (4) Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung Bremerhaven, Germany

The boron isotope (δ^{11}B) composition of marine calcifiers is considered to be one of the most reliable pH proxies, enabling us to reconstruct past ocean pH and infer on the associated changes in carbon budget involved (e.g. Gutjahr et al. 2017). The application of the commonly used δ^{11}B archives such as foraminifera or corals is however mostly limited to the Cenozoic due to insufficient preservation or incomplete geological records. Brachiopods have a promising potential for extending our knowledge on seawater pH evolution throughout the entire Phanerozoic considering their high abundance in the fossil record and its origin dating back to the early Cambrian. Moreover, their shell is composed of low-magnesium calcite, rendering brachiopods more resistant to post-depositional diagenetic alteration of its primary chemical signal (e.g. Brand et al. 2012). Additionally, even today they present an extant and widespread taxa, allowing for an assessment of the controls on boron isotope incorporation into brachiopod calcite and possible distortions of the signal due to vital effects or other processes.

We present a detailed exploration of boron isotope systematics in three different brachiopod species (*Magellania venosa*, *Terebratella dorsata*, *Pajaudina atlantica*) cultured under controlled laboratory settings for over a year. Our experimental setup includes a control (pH = 8.15) and two pH treatments (pH = 7.6 and 7.35), and we provide both bulk MC-ICP-MS as well as high spatial resolution SIMS data of the shell material. Our results indicate that boron incorporation is primarily driven by vital effects related to their ability to regulate calcifying fluid pH in response to ambient changes, which we further validate by in vivo microelectrode measurements (e.g. Stumpp et al. 2012). Despite internal buffering, the local pH at calcification sites systematically decreases with seawater pH, and hence is impacted by ocean acidification. This not only suggests that brachiopod shells serve as useful and conservative recorders of past ocean pH trends, but also provides new insights into mechanisms that may have enabled brachiopod survival throughout several major environmental crises in the past.

Our findings have implications for past climate studies, as well as research on calcification processes and physiological adaptations to environmental change (e.g. the actual global ocean acidification).

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