



## **Variations in the boron isotopic and elemental composition in modern brachiopods: Assessing the biomineralization processes in the shell microstructure.**

Sara Ana Milner Garcia (1), Claire Rollion-Bard (1), Jan Fietzke (2), Pierre Burckel (1), Adam Tomašových (3), and Daniela Henkel (2)

(1) Institut de Physique du Globe de Paris, Paris, France (milner@ipgp.fr), (2) GEOMAR Helmholtz-Zentrum für Ozeanforschung, Kiel, Germany, (3) Earth Science Institute, Slovak Academy of Sciences, Bratislava, Slovakia

The boron isotope composition (commonly expressed as  $\delta^{11}\text{B}$ ) of marine calcium carbonate is one of the most reliable pH proxies (e.g. Vengosh et al., 1991; Hemming and Hanson, 1992). In this context, brachiopods are a potential archive due to their great abundance in the geological record and their low-magnesium calcite shells that make them more resistant to diagenetic alteration (e.g. Lowenstam, 1961; Veizer et al., 1986). This study focuses on the impact of brachiopod shell biomineralization processes on the boron isotopic and elemental (B/Ca) compositions. Boron isotope analyses were performed at the micrometer scale by ion microprobe, and by laser ablation (LA) coupled to a MC-ICP-MS to create 2D images, while B/Ca was determined using LA-ICP-MS in shells of five modern brachiopods species composed of primary (PL) and secondary layer (SL) (*Terebratalia transversa*, *Magasella sanguinea*, *Notosaria nigricans*, *Calloria inconspicua* and *Magellania venosa*) and one species composed also with tertiary layer (TL) (*Liothyrella neozelanica*). Our results show that the PL is slightly depleted in  $^{11}\text{B}$  relative to the SL and higher in B/Ca. The SL layer does not show a specific trend of  $\delta^{11}\text{B}$  from the outermost to the innermost shell thickness. B/Ca ratio goes towards lower values in the innermost regions of the shell likely due to kinetic effects, as less boron is incorporated as growth rates slow. Values obtained here are similar to those previously published (Lécuyer et al., 2002; Penman et al., 2013). Regarding the TL, B/Ca values are lower than in PL and SL. We will further explore the mechanisms responsible for such differences in  $\delta^{11}\text{B}$  and B/Ca values between the different shell layers and its potential use as palaeo-pH proxy.

Hemming, N., Hanson, G., 1992. Boron isotopic composition and concentration in modern marine carbonates. *Geochim. Cosmochim. Acta* 56, 537–543.

Lécuyer, C., Grandjean, P., Reynard, B., Albarède, F., Telouk, P., 2002.  $^{11}\text{B}/^{10}\text{B}$  analysis of geological materials by ICP-MS Plasma 54: application to the boron fractionation between brachiopod calcite and seawater. *Chem. Geol.* 186 (1–2), 45–55.

Lowenstam, H.A., 1961. Mineralogy, O-18/O-16 ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans. *J. Geol.* 69, 241–260.

Penman, D.E., Hönisch B., Rasbury E.T. Hemming, N.G., Howard J.S., 2013. Boron, carbon, and oxygen isotopic composition of brachiopod shells: Intra-shell variability, controls, and potential as a paleo-pH recorder. *Chem. Geol.* 340, 32–39.

Veizer, J., Fritz, P., Jones, B., 1986. Geochemistry of brachiopods: oxygen and carbon isotopic records of Paleozoic oceans. *Geochim. Cosmochim. Acta* 50, 1679–1696.

Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A.R., McCulloch, M.T., 1991. Co-precipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochim. Cosmochim. Acta* 55, 2901–2910.