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Assessing the biomineralization processes in the shell microstructure of modern brachiopods: variations in the oxygen isotope composition and minor element ratios

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Brachiopods have been extensively used to reconstruct physicochemical conditions of ancient oceans due to their extensive fossil record and shells made of stable low-Mg calcite. In this context, it is important to assess the impact of brachiopod shell biomineralization processes on geochemical proxies.
Six modern species of brachiopod specimen representing the three low-Mg calcite orders (i.e. Terebratulida, Rhynchonellida and Thecideida) were selected, in order to identify the most reliable taxa and the best shell portions to use for measurements of proxies. Three main different shell structures were identified: (1) only primary layer, (2) primary and secondary fibrous layers and (3) same as (2) with also a tertiary columnar layer.
Oxygen isotope composition was measured at the micrometre scale with high-resolution ion microprobe. Generally, O isotope values of shells composed of primary and secondary layers show a progression towards more positive values from the outer primary layer to the inner secondary layer. The columnar tertiary shell layer, when present, has the most positive isotopic O values, the closest to the isotopic equilibrium. Variations at the micrometre scale are higher than those measured by conventional bulk techniques, as already shown by Cusack et al. (2012).
Trace elements ratios (Li/Ca, B/Ca, Na/Ca, Mg/Ca, and Sr/Ca) were determined by laser ablation coupled to an ICP-MS. The trace element points define profiles parallel to the O isotope ion probe spots. The elemental ratio profiles of species composed by primary and secondary shell layers (*Terebratalia transversa, Magasella sanguinea* and *Magellania venosa*) show different behaviours depending on the elements. Mg/Ca and Sr/Ca values are constant throughout all profiles, even Mg/Ca values are more variable. The values of both ratios are in good agreement with previous studies (Perez-Huerta et al., 2008; Butler et al., 2015). Li/Ca values are also constant among the different profiles. In contrast, while B/Ca values in the secondary layer are constant, the primary layer is eventually enriched in some profiles. Na/Ca ratio in *M. venosa* is higher in the primary layer while the other species are not. In shells comprising a columnar tertiary shell layer (*Liothyrella neozelanica* and *Gryphus vitreus*) there is a depletion of all the trace elements measured, indicating that different biomineralization mechanisms influence the fractionation of the elemental ratios in the different shell microstructures. Moreover, while the columnar layer seems a good target for O isotope measurements, the very low content of trace elements in this columnar calcite makes difficult its use for paleoenvironmental proxies (ratios and isotopic composition of minor elements). We will explore further the mechanisms responsible for such differences of elemental and isotopic ratios between the different shell layers.