Imaging of Boron Isotope Distribution in Brachiopods using LA-MC-ICP-MS

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Reconstruction of the Phanerozoic seawater chemistry is of major interests in marine geochemistry. Chemical signatures in carbonate hard parts of marine calcifying organisms are used as proxies for reconstructions of parameters like temperature, salinity or pH. In particular boron isotopes have been established as seawater pH proxy.

Brachiopods are widely used as a fossil archive for the above mentioned reconstruction. The precipitated parts of their shells have proved to be formed in equilibrium with seawater composition (e.g. oxygen isotopes) and are reliable records of radiogenic Sr isotopes, as well. Nevertheless, in the case of the application of boron isotopes as pH proxy, only first preliminary calibrations do exist for brachiopods.

Boron isotopes are commonly analyzed using bulk techniques (e.g. TIMS or MC-ICP-MS). Those techniques hardly allow for a detailed investigation of the spatial distribution of boron including its isotopic composition within complex samples like biogenic shells or skeletons.

In our study we used the shell of *Terebratella Sanguinea* brachiopod samples, collected alive from New Zealand shores. The shell samples were sectioned, polished and analyzed using electron microprobe (EMP) collecting the elemental maps of Ca, Mg, Sr and S. Boron elemental and isotopic distribution was determined as 2D images (resolution of 25 µm) using LA-MC-ICP-MS. This approach allows for unique insights into the complexity of boron distribution on the µm scale. Our results show a huge degree of intra-shell variability. Boron concentration varies by almost a factor of 5, like the boron isotopic ratio which varies over ~15 ‰.

The acquired images reveal how this considerable variability of boron and its isotopes are correlated to the structural features of the shell. For example, the secondary layer displays a large variability in boron concentration and remarkably light isotopic signatures (down to ~ 5 ‰). In contrast, the primary layer has been found to be a lot more homogenous and appears to reflect the boron isotopic composition of the ambient seawater borate, making this part of brachiopod shells a promising candidate for pH reconstruction.