

EGU2020-13080

<https://doi.org/10.5194/egusphere-egu2020-13080>

EGU General Assembly 2020

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The effect of high pCO₂ on trace elements and intrashell variability: A culture experiment with live benthic foraminifera.

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We cultured two species of *Amphistegina* under four pCO₂ concentrations yielding variable pH (8.1–7.6) and DIC (2340–2570 μM) at constant temperature (25 °C) and alkalinity (~ 2500 μM). To mark the newly grown shells under the experimental conditions we spiked the culture seawater with ¹³⁵Ba. The variability of trace elements within the foraminiferal shells was measured on three individuals of each species for each treatment using LA-ICPMS in the knob area. Sharp transition zones were observed between the natural and the ~tenfold increased ¹³⁵Ba in the shells. The shape of the transition zone is best described by a logistic equation for population growth. We propose that this reflects the dynamics of seawater vacuoles population that serve the biomineralization process and provide Ca and DIC for calcification of *Amphistegina* as described in previous publications (e.g. Bentov et al., 2009). In individuals that showed significant growth (identified by ¹³⁵Ba-enriched shell), B, Na and Sr showed a significant increase with DIC, while K and Mg were slightly lower or unchanged. LA-ICPMS profiles in the central knob (~70 μm depth) also revealed previously described cyclical changes in concentration of Mg, each apparently representing a growth of a new chamber. Additional elements such as K, Na and U showed similar cycles with the same frequency and phase as the Mg cycles. Sr showed variability with similar frequency but not in-phase with those of the Mg. These multi-element cycles were found both in the newly grown calcite (elevated-¹³⁵Ba and pCO₂) and in the natural skeleton regardless of the pCO₂ treatments. These high Mg and multi-element cycles seem to be an essential part of the calcification process. They may originate from the interaction with the organic matrix resulting in elevated Mg and other elements in the primary calcite while secondary calcite of the lamination process shows lower concentrations. It is also possible that primary calcite is enriched in trace elements if an Amorphous CaCO₃ (ACC) or vaterite precursors are involved. In addition, Rayleigh fractionation from a semi-closed reservoir, the presence of high Mg in the lattice or any combination of the previous causes may explain the trace elements enrichment. While changes in the pCO₂ did change the average concentrations of B, Na, and Sr, they did not affect the banding of trace elements in these foraminifera, suggesting that these cycles are inherent to the biomineralization process.

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