The effect of high pCO\textsubscript{2} on trace elements and intrashell variability: A culture experiment with live benthic foraminifera.

Adam Levi\textsuperscript{1}, Wolfgang Müller\textsuperscript{2}, and Jonathan Erez\textsuperscript{1}

\textsuperscript{1}Institute of Earth Sciences, the Hebrew University of Jerusalem, Israel (adam.levi@mail.huji.ac.il)
\textsuperscript{2}Institute of Geosciences, Goethe-University, Frankfurt am Main, Germany

We cultured two species of Amphistegina under four pCO\textsubscript{2} 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 \textsuperscript{135}Ba. 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 \textsuperscript{135}Ba 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 \textsuperscript{135}Ba-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-\textsuperscript{135}Ba and pCO\textsubscript{2}) and in the natural skeleton regardless of the pCO\textsubscript{2} 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 CaCO\textsubscript{3} (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 pCO\textsubscript{2} 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.