Climate Center grant report: Evaluating the potential of boron isotopic composition of brachiopod calcite as a proxy for Phanerozoic seawater pH and secular variation in $\delta^{11}B_{seawater}$

In November 2008 we were funded $8000 dollars by the Climate Center to study the variation of boron isotopes in modern brachiopod shell calcite, with the goal of evaluating their potential as recorders of ancient seawater pH, thus extending the boron isotope pH proxy potentially to the entire Phanerozoic. To this end we acquired a loan of modern brachiopod shells from the American Museum of Natural History from throughout the modern ocean. We measured 4 microsampled transects through two shells of two different species, and based on observed trends sampled 9 additional shells of 4 different species. Each of these samples was analyzed for boron isotopic composition on Lamont's Triton Thermal Ionization Mass Spectrometer. Additionally, the sample transects were analyzed for C and O isotopic composition at UC Davis. Perhaps the most important result of our research is the intrashell variation revealed by the transects. In both species, we observed heavily depleted $\delta^{11}B$ values in both the exterior and interior margins of the shell, with higher, relatively stable values in the innermost regions of the shell (the midpoint, with respect to thickness). In this innermost region, we found little to no variation along the length of the shell, including hinge material. Our C and O transects agree strongly with previous studies, finding equilibrium values in the interior and most of the secondary layer, with depleted values in the exterior part of the secondary layer and the primary layer. There is a high level of correlation between C and O values, suggesting that a common, probably kinetic fractionation is responsible for the observed trends. There is also a slightly worse but quite significant correlation between those systems and B isotope values, suggesting that this kinetic fractionation may be the cause of some of the B variation, although the trend is markedly different in the interior regions of the shell: B values become heavily depleted whereas C and O are at their highest equilibrium values. The implications of these trends are two-fold: most important, we now know how to correctly sample brachiopod shells for boron isotopes: only the innermost calcite records a stable, non-depleted value. Secondly, it provides a test for B-alteration in ancient specimens: if the observed trend is present, we know the B is primary.

Comparison of the $\delta^{11}B$ values to local pH calculated from ocean carbonate chemistry data indicates that there is a strong dependency of boron isotopes on pH. There appear to be large offsets from foraminifera calibration curves and between brachiopod species, but largely we have shown that the proxy does work. We are currently preparing these results for publication, and they should form the basis of further proposals applying the proxy to deep time. This has been a large first step towards reconstructing seawater pH and CO2 levels throughout the Phanerozoic.