Boron in soil carbonates: a soil CO_2 proxy

D.O. BREECKER[1] H. FRICKE[2], C. J. MCNEECE[1], N. MILLER[1], M. F. SCHALLER[3], W. CLYDE[4]

[1]The University of Texas at Austin; breecker@jsg.utexas.edu
[2]Colorado College
[3]Rensselaer Polytechnic Institute
[4]The Univeristy of New Hampshire

The boron isotope composition of planktic foraminiferal calcite records paleo seawater pH, which helps to quantify paleoatmospheric CO_2. This proxy is based on the pH-dependent speciation of B in aqueous solution. Here we extend this theory to the freshwater-carbonate system of soils. In calcite-bearing soils, porewater pH varies with soil CO_2 concentrations, and thus boron in soil carbonate should record soil CO_2. Such an independent soil CO_2 proxy could be useful for studying changes in aridity and, when used alongside $\delta^{13}C$ values, changes in paleoatmospheric CO_2.

Because a substantial fraction of boron in soil porewaters is typically sorbed onto particle surfaces, we speciating boron with PHREEQC, using the constant capacitance model, equilibrium constants appropriate for fresh water, and surface complexation constants from the literature. The inclusion of complexation narrows the range over which boron speciation is pH-dependent, suggesting that soil carbonate boron is a very sensitive pH proxy between 7.5 to 9. We apply the theory to successions of paleosols by finding the factor soil CO_2 change required to explain measured shifts in both [B] and $\delta^{11}B$ values of paleosol carbonates. The calculated factor soil CO_2 change is sensitive to temperature but not to soil surface area or to the values of the complexation constants.

We applied this soil CO_2 proxy to a sequence of paleosols spanning two early Eocene hyperthermal events (ETM2 and H2) from the central Bighorn Basin. [B] measured by ICP-MS tracks nodule $\delta^{13}C$ values closely through both hyperthermals, with low [B] (< 5 ppm) during the peak of negative carbon isotope excurions (CIE) and higher baseline values of 10 ppm before and between excursions. At three statigraphic levels high [B] (up to 25 ppm) depart from these trends and are associated with elevated Fe. The carbonate nodule $\delta^{11}B$ values measured thus far (by MC-ICP-MS) decrease from 10‰ before ETM2 to 2‰ at the peak of the ETM2 CIE. These results are consistent with an increase of soil CO_2 during these hyperthermals. For ETM2, application of our theory assuming no temperature change suggests soil CO_2 concentrations increased by a factor of 10x, which corresponds to a 6x increase in atmospheric CO_2. Consideration of warming during ETM2 would increase these factors.