

Seasonal variability in B speciation and B/Ca in planktonic foraminifera from the Cariaco Basin, Venezuela

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We determined B/Ca on four planktonic foraminiferal species (*Globigerinoides ruber*, *Globigerinoides sacculifer*, *Orbulina universa*, and *Globorotalia menardii*) on a Thermo Element 2 high resolution ICP-MS. The material is from biweekly sediment trap samples collected in Cariaco Basin, Venezuela (10°30' N, 65°31' W) over a three year period between May 2003 and May 2006. The data are compared to local hydrography and water column chemistry to evaluate environmental controls on B incorporation into foraminiferal calcite. In addition, seasonal variability of B speciation in the foraminiferal calcite is assessed using ¹¹B magic angle spinning (MAS) nuclear magnetic resonance (NMR) on samples of *O. universa* from January, February, and April 2007 and of *G. menardii* from December 2006. The B/Ca (μmol/mol) data displays clear depth stratification with the surface dwelling *G. ruber* having the highest B/Ca, followed by *G. sacculifer* and the deeper dwelling *G. menardii* and *O. universa* having the lowest, consistent with a decrease in pH with depth. The data also show a repeatable seasonal pattern with the highest values occurring when the water column is stratified in June and July and the lowest occurring during upwelling in December and January. However, none of the environmental variables have a strong correlation with B/Ca. The ¹¹B MAS NMR *O. universa* data show a seasonal change in the speciation of B within the foraminiferal calcite. During January the boron is almost entirely incorporated (~90%) in a previously unrecognized trigonal form. However, in April only ~75% of the boron is in this trigonal form, whereas the rest of the boron is divided evenly between borate and boric acid. The observed trigonal form has a C_q of 3.0, which is similar to the theoretical value of 3.15 [1] for the corner-sharing borate carbonate complex, B(OH₂)CO₃⁻. It is hypothesized that during calcification boron is converted to a borate carbonate complex, which is ultimately converted to either borate or boric acid with each equally likely [1, 2]. Our results support this hypothesis except that most of the boron does not complete this reaction, but remains in the intermediate borate carbonate complex form.

[1] Tossel (2006) *Geochimica et Cosmochimica Acta* **70**, 5089-5103. [2] Klochko et al. (2009) *Geochimica et Cosmochimica Acta* **73**, 1890-1900.

Natural sources of uranium in shallow groundwater in Northeastern Alberta

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Elevated dissolved uranium (U) concentrations up to 170 μg L⁻¹ were measured in shallow (<25 m depth) domestic water wells near Bonnyville, Alberta. This area of Alberta is covered in glacial till deposits up to 200 m thick with several regional interglacial sand and gravel aquifers. Sediment coring for mineralogical analyses and installation and monitoring of nested piezometers were conducted at two sites to determine the source of U in shallow aquifers in the area. Field observations indicated that the till at both sites showed signs of oxidation at depths down to 6 m, suggesting that the primary source of U in the shallowest underlying aquifer may be from weathering and leaching of overlying U-bearing minerals. Speciation modelling showed that porewater was undersaturated with respect to secondary U minerals in the vadose zone, but that groundwater became saturated with respect to secondary U-hydroxide minerals with depth as conditions became more reducing. The dominant U complexes in groundwater were found to be U-hydroxides for U(IV) species and uranyl carbonates for U(VI) species.

The quantitative mineralogical study included analyses of the oxidized and unoxidized till, aquifer sediments and secondary precipitate samples. No major mineralogical differences were observed between the till and sand sediments other than a higher proportions of dolomite and clay minerals present in the till samples. The major U carrier for both sediments was zircon. Two types of U-bearing zircons were observed, with the highest U concentrations up to 4500 ppm coming from the samples showing characteristics of metamict zircon, possibly altered at near-surface conditions in the oxidized till. The other type was a near-end-member zircon, which was observed more frequently in the unoxidized clay-till. A secondary precipitate collected from a plumbing fixture at one site exhibited elevated concentrations of U consisting of Ca-rich carbonates such as monohydrocalcite, which was likely acting as a sink for U. XANES characterization indicated that U is present as U(VI) coprecipitated with carbonate minerals. ²³⁴U/²³⁸U isotope ratios measured in groundwaters showed minimal variability between the two sites despite variations in U concentration and with depth suggesting a regional source rather than a point source. The combined results did not show any evidence of an anthropogenic source of U, but suggest that alteration of metamict zircon naturally present in near-surface environments (at near neutral pH and low temperatures) could result in the release of dissolved U, leading to elevated U concentrations observed in local groundwater.