Isotopic composition of boron adsorbed on amorphous silica

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The boron abundance and isotopic composition of marine carbonates have been extensively used for paleo-climate reconstructions. Boron is also incorporated by the skeletons of siliceous organisms such as sponges, diatoms and radiolarians, where it can be present in amounts above a thousand ppm. Reported $\delta^{11}B$ values of marine biogenic silica vary between 2 and 25 ‰, suggesting that the B isotopic composition of these organisms could be used for paleo-environmental reconstructions in the same way as biogenic (corals and foraminifera) or inorganic carbonate minerals.

To shed light on the mechanisms that govern the uptake of B by siliceous organisms and its isotopic composition, we measured the adsorption of this element at the surface of amorphous silica in NaCl aqueous solutions as a function of pH, and determined the isotopic fractionation between the solid surface and the fluid. The modelling of the experimental data shows that both $B(OH)_3^0$ and $B(OH)_4^-$ are adsorbed onto SiO_2(am). Trigonal boron was found to form an inner-sphere complex whereas the borate ion forms inner- and outer-sphere complexes with the silica surface functional groups. Inner-sphere B(III) and B(IV) surface species were found to be enriched in ^{10}B by 13 and 12 ‰, respectively, compared to their aqueous counterparts, as opposed to the B(IV) outer-sphere complex, which appeared to be ~ 6 ‰ heavier than aqueous borate.

Some experiments were also carried out using $CaCl_2$ as background electrolyte. The adsorption of B increased by a factor of ~2 compared to NaCl and the corresponding isotopic data are consistent with the sorption of only tetrahedral boron at the SiO_2(am)/fluid interface.

The apparent complexity of sorption reactions requires further investigations to better understand the mechanisms that control B incorporation and isotopic signature in biogenic silica and to develop a new proxy for paleo-environmental conditions and biogeochemical processes.