Molecular simulation of pressure dependent boron isotope equilibrium between boron hydrates

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Boric acid, $B(OH)_3$, is partially dissociated in solution as borate anion, $B(OH)_4^-$. Boron, B, isotope exchange equilibrium between the two B species has been an important tool to study geochemical problems related to circulation of volatile elements at subduction related environments. Since chemical equilibrium depends on several factors, however, careful discussion on B isotope fractionation in nature is required. Recent results on molecular orbital, MO, calculations showed that the reduced partition function ratio, RPFR, of B hydrate depended on the hydration number. Since pressure promotes dehydration of hydrates adsorbed onto the solid phase, it may affect the B isotope effects.

In this study, we performed the molecular dynamics, MD, simulation to evaluate the pressure dependence of dehydration of B hydrates in solution, employing the MPDyn program. After the geometrical parameters and force fields of molecules were calculated by the *ab initio* MO method, the systems of a $B(OH)_3$ molecule with 2502 H_2O molecules, and a $B(OH)_4^-$ ion and a H_3O^+ ion with 2500 H_2O molecules were simulated. The simulations were performed for 10 ps at 100 MPa, and for 100 ps at 0.1, 50, and 100 MPa. The radial distribution function, RDF, and the angle distribution were calculated for 1.2 ns.

Results on the RDFs show that the hydration numbers in the first hydration sphere, n_1, are invariant up to 100 Mpa both for $B(OH)_3$ and $B(OH)_4^-$, which indicates that pressure little influences the B isotope effects caused by dehydration of the boron hydrates in bulk solution. On the other hand, a MO study indicated that the RPFR of $B(OH)_4^-$ increases with decreasing n_1 of $B(OH)_4^-$ hydrate adsorbed onto the solid phase, meaning that dehydration of B hydrate during adsorption onto the solid phase from bulk solution phase could reduce its RPFR. It is thus suggested that the pressuredependent B isotope effects will be significant if pressure enhances the dehydration of $B(OH)_4^-$ hydrate during adsorption.