

Boron Isotopic Fractionation During Oxide Sorption: Application for Past Oceanic pH Estimation

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Boron (B) isotopic compositions in marine carbonates have been widely applied for reconstruction of oceanic pH in the past. However, these studies have assumed constant B isotopic compositions in the ocean and no significant isotopic fractionation has occurred during sorption/precipitation of B in marine carbonates. In this study, we have evaluated in detail of the B and $\delta^{11}\text{B}$ sorption behavior using FeCr_2O_4 nanoparticles in seawater-like matrix at various pH conditions, aimed to explore new possibility to apply B and $\delta^{11}\text{B}$ in oxide phases and clays for environmental reconstruction. The distribution coefficient (Kd) of boric acid and the associated fractionation factors ($\alpha_{3/4}$) as a function of solution pH were examined systematically and precisely determined. It is evident that the Kd values were critically depended on the boric speciation in solution, as well as the surface characteristics of minerals, and followed a linear trend at pH 6~8. At higher pH, Kd decreased sharply from 50 to zero (pH 10~12). On the other hand, the isotopic fractionation factors increased gradually with pH, $\alpha_{3/4}$ of 0.975 and 1.098 at pH 6 and 12, respectively. The isotopic differences between solids and liquids ($\Delta^{11}\text{B}$) display an excellent linear relationships with the pH, $\Delta^{11}\text{B} = 4.8295 \cdot \text{pH} - 45.677$ $R^2 = 0.9833$, under the designed experimental conditions. The observed large, but linear fractionation of $\delta^{11}\text{B}$ in solutions make B isotope a potential sensitive proxy for studying solution pH during oxide mineral adsorption.