Boron isotopic fractionation during carbonate precipitation

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The boron isotopic composition of marine carbonates has been expected as a promising proxy for the paleo-seawater pH.[1] Boron has two aqueous species in seawater: $B(OH)_3$ and $B(OH)_4^-$, and the relative abundances depend on pH. Magnitude of boron isotopic fractionation between the two species was theoretically calculated, resulting in ca. 20‰.[2] To interpret boron isotopic composition preserved in carbonates to pH of seawater, it has been often assumed that only $B(OH)_4^-$ is incorporated into the carbonates, and no isotopic fractionation occurs on boron during uptake. In this study, to verify these assumptions, we examined boron isotopic fractionation factor during carbonate precipitation by experimental approach.

Boron-doped calcium carbonates (aragonite and calcite) were synthesized under controlled pH condition, and $\delta^{11}B$ of those was measured by MC-ICP-MS (Nu plasma).

Resulting $\delta^{11}B$ of precipitated inorganic aragonite increases systematically as pH increases. Moreover, obtained pH-$\delta^{11}B$ plot forms a curve to be paralleled to the calculated value. [2] Interestingly, the curve is not similar with theoretical one but lies lower by 4‰ than that. This offset suggests that boron is incorporated into aragonite as $B(OH)_4^-$ and ca. -4‰ isotopic fractionation occurs through the process. In addition, we preliminarily observed higher $\delta^{11}B$ in calcite than in aragonite. Crystal structure of carbonate might influence on magnitude of isotopic fractionation associated with uptake process of boron.

[1] Vengosh et al., *GCA,* **55**, 290 (1991)
[2] Kakihana et al., *Bull. Chem. Coc. Jpn*. **50**, 158 (1977)