Interface interaction and associated boron isotope fractionation in a steady-state carbonate-seawater system

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Since the pioneer work of Vengosh et al. (1991) and Hemming and Hanson (1992) [1, 2], the boron isotope paleo-pH proxy has been advancing rapidly as one of the most promising tools for reconstructing the past changes in ocean pH and atmospheric CO_2 and constraining potential drivers of that changes. Together with the proxy of B/Ca ratios, the implications of these geochemical proxies provide new insight into the evolution of atmospheric CO_2 concentrations at time scales from tens of millions to thousands of years. Meanwhile, major concerns related to the fundamentals of these proxies have been raised.

The study on the interface reactions and boron isotope fractionation in a steady-state carbonate-seawater system has shown that: (i) carbonate crystals do not precipitate even when the solution reaches saturation and the presence of carbonic anhydrase enzyme can promote the process, indicating the precipitation kinetics of inorganic carbonates from natural seawater is fairly slow; (ii) both theoretical and experimental evidence prove that the charged $B(OH)_4^-$ ions adsorb preferentially over H_3BO_3 onto positively charged calcite crystal surfaces and finally co-precipitate into occlusions or inclusions after formation of new layers of calcites; (iii) the Langmuir isotherm well describes the adsorption process, yielding an equilibrium constant K of 0.0053 ± 0.0003 and the maximum adsorption capacity $[B]_{solid\text{-}max}$ of 71.4-418 $\mu g \cdot g^{-1}$ for calcite and aragonite, covering the variation of boron contents in a variety of biogenic carbonates; (iv) the boron isotope fractionation value of $\alpha_{4\text{-}3} = 0.974 \pm 0.004$ in calcite-seawater system further confirms the selective incorporation of charged $B(OH)_4$ species in calcite.

[1] Vengosh A., et al. (1991) Geochem. Cosmochim. Acta 55, 2591–2606.

[2] Hemming N.G., Hanson G.N. (1992) Geochem. Cosmochim. Acta 56, 537–543.