Towards a General Model for B incorporation in $CaCO_3$

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The boron isotopic composition ($\delta^{11}B$) and abundance (B/Ca) in the marine carbonate minerals calcite and aragonite ($CaCO_3$) are used as paleoceanographic tracers for past oceanic pH and carbon chemistry. These proxies rely on a systematic relationship between the B content of $CaCO_3$ and the B and C chemistry of the parent solution. This relationship was originally proposed to be the sole uptake of $B(OH)_4^-$ from solution into the mineral phase with negligible isotopic fractionation. However, recent inorganic precipitation experiments measuring both B/Ca and $\delta^{11}B$ offer strong evidence to suggest that B incorporation is more complex, with apparent sensitivity to numerous aspects of solution chemistry and crystal growth. Additionally, theoretical and experimental studies of B adsorption suggest the potential for isotopic fractionation during B incorporation. These processes have the potential to influence the B chemistry of $CaCO_3$, and are significant sources of uncertainty for the B proxies that need to be constrained.

We have developed a model of B incorporation in $CaCO_3$ based on DePaolo's Surface Kinetic Model[1], which parametrises impurity incorporation relative to the attachment and detachment of 'host' ions from the crystal surface using 'forward' and 'backward' partitioning coefficients. By considering the interaction of both $B(OH)_4^-$ and $B(OH)_3$ with the crystal surface, our model is able to predict the B/Ca and $\delta^{11}B$ of all published inorganic calcite precipitation data. The optimised model parameters suggest that $B(OH)_4^-$ is the primary incorporated species into calcite, with a minor contribution of $B(OH)_3$ that is sensitive to both solution chemistry and precipitation rate. Minor deviations between the model and data imply second-order processes, such as isotopic fractionation during incorporation and evolved surface boundary layers, which can also influence B incorporation, and can be incorporated to improve the model.

This model provides a quantitative framework to understand B incorporation in $CaCO_3$, and highlights key parameters in mineral precipitation that have the potential to influence the B geochemistry of $CaCO_3$.

[1]DePaolo (2011) doi:10.1016/j.gca.2010.11.020