

Boric acid diffusion in biomineralisation: implications for B geochemical proxies.

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The abundance and isotopic composition of boron in carbonate biominerals are interpreted as records of carbon chemistry and pH in either seawater, the calcifying fluid, or some combination of the two. These interpretations of B geochemistry all rely on the key assumption that the concentration and isotopic composition of total B in the calcifying fluid is the same as external seawater.

Boric acid is a small, neutral molecule that can diffuse easily across biological membranes. The diffusive transfer of $B(OH)_3$ between seawater and the calcifying space provides an isotopically-distinct B-specific transport pathway between seawater and the calcifying fluid. The importance of this pathway depends on pH gradients between these environments, and the dynamics of ion transport to the calcifying space. This previously unaddressed process has the potential to substantially alter both the concentration and isotopic composition of B in the calcifying fluid compared to seawater, calling the key assumption behind our interpretation of biomineral B geochemistry into question. How can we tell if this process is important, and how could it alter our interpretation of B geochemistry?

We explore these questions using a steady-state model of B transport and incorporation in biomineralisation. Three key fluxes dominate biomineral formation: $CaCO_3$ precipitation, the exchange of seawater with the external environment, and ion transport across membranes by diffusion or active pumping. By reducing the problem to the balance between these three key fluxes, it is possible to explore a wide range of biomineralisation scenarios with minimally restrictive assumptions. Within this framework, we consider both the transport of $B(OH)_4^-$, and the transport and passive diffusion of membrane-permeable $B(OH)_3$, allowing us to explore a comprehensive range of candidate biomineralisation scenarios and B transport processes.

Our model offers two key insights into our interpretation of the boron proxies:

1. We identify biomineralisation conditions necessary for B geochemistry to record external seawater conditions, despite modified pH and carbon chemistry at the calcification site.
2. We show that B geochemistry alone does not uniquely constrain the pH and carbon chemistry at the site of calcification.