

EGU2020-21988

<https://doi.org/10.5194/egusphere-egu2020-21988>

EGU General Assembly 2020

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Boron proxies and biomineralisation: the possible, the impossible and the likely.

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The abundance and isotopic content of boron in carbonate biominerals provide our best records of ocean carbon chemistry and pH, which have proved instrumental in studying past episodes of CO₂-induced climate change. The boron proxies are based on the theory that carbonates solely incorporate B(OH)₄⁻ in proportion to seawater B(OH)₄⁻/HCO₃⁻ or B(OH)₄⁻/CO₃²⁻, capturing both the state of the ocean C system and the pH-dependent isotopic composition of B(OH)₄⁻. However, models of biomineralisation invoke significant modification of internal carbon chemistry to facilitate calcification, and substantial proton export has been observed during carbonate formation. The pH, carbon and boron chemistry at the site of calcification cannot be the same as that of external seawater. How, then, do biominerals appear to record seawater B(OH)₄⁻? While unanswered, this question raises serious problems for our interpretation and use of the B proxies.

We explore this question using a quantitative model of B transport and incorporation in biomineralisation. Three key fluxes dominate biomineral formation: CaCO₃ 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.

By explicitly including the independent transport of both B species, our model offers two key insights into the mechanisms behind the boron proxies and biomineralisation:

- We identify biomineralisation mechanisms that allow B geochemistry to record external seawater conditions, despite the modified chemistry at the calcification site.
- We constrain the dynamics of the calcification environment (e.g. 'closed' vs. 'open' or Rayleigh- vs. transport-dominated system) by inverting the model to consider paired B/Ca and δ¹¹B data, offering key new constraints on ion transport processes in biomineralisation.