Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.27524

Interaction of bioaragonite with aqueous solutions bearing P and P-S under soft hydrothermal conditions

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Phosphorite deposits are a primary source of phosphorus, a crucial element for fertilizer production and thus for global agricultural sustainability. These phosphate-rich sedimentary rocks form predominantly in shallow marine environments, where the circulation of fluids within centimeters beneath the sediment-water interface triggers mineral reactions that continue to progress during diagenesis. Different researchers have suggested that the interaction of calcium carbonates with aqueous solutions rich in P controls the bioavailability of this element in natural settings where sedimentary carbonates are abundant[1]. Dissolved phosphorus in marine systems is not only essential for sustaining biological productivity but also plays a critical role in linking the global phosphorus and carbon cycles, thereby influencing both marine ecosystem dynamics and long-term climate regulation. Here, we examine the interaction between bioaragonite (*Cerastoderma edule*) and a phosphate-rich aqueous solution or a mixture of phosphate- and sulphate- rich aqueous solutions by monitoring both evolution of chemistry of the aqueous solution and mineralogical changes in the solid phases.

Our results show a rapid decrease of P concentration accompanied by an increase of both calcium concentration and pH in the aqueous solution. Regardless of the initial experimental conditions, hydroxylapatite is the first phase to precipitate and the only phase detected in experiments conducted at 60ºC, as confirmed by XRD and FTIR analyses. However, upon aging, calcite formation is observed in experiments conducted at 80ºC. The presence of sulfate in the aqueous solution accelerates the precipitation of calcite and modifies its morphology as observed by SEM. The evolution of the system suggests a coupled bioaragonite dissolution and precipitation of calcite and/or hydroxylapatite in proportions that vary with time and temperature. We interpret the precipitation sequence by considering the dissolution kinetics of bioaragonite along with the stoichiometry and solubility of all secondary phases.

[1] Glenn, Föllmi, et al., (1994). *Eclogae Geologicae Helvetiae, 87 (3), 747-788*