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Why does aqueous phosphate inhibit aragonite nucleation?

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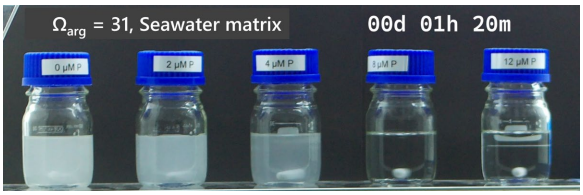

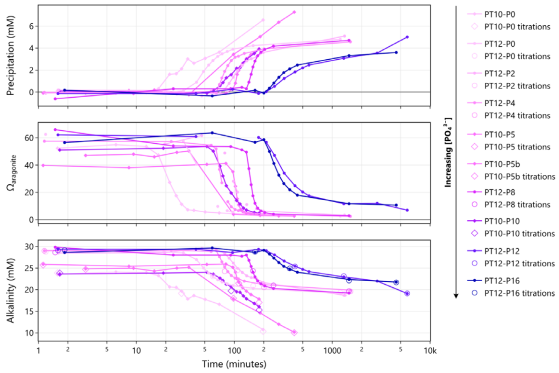

Throughout geological history, Earth's oceans contained varying amounts of chemical species which kinetically inhibit the precipitation of carbonate minerals. By altering the threshold at which carbonates begin to form, inhibitors influence seawater chemistry, carbon cycling and the carbonate rock record – for example, inhibition of calcite precipitation by Mg^{2+} resulted in the familiar pattern of calcite and aragonite seas through the Phanerozoic. It has been hypothesised that, during certain intervals of the Precambrian, both calcite and aragonite precipitation were inhibited in the oceans [1]. This would permit significantly increased alkalinity and carbonate supersaturation, opening the possibility for non-classical crystallisation of carbonates *via* metastable precursors, potentially explaining enigmatic minerals and fabrics in Precambrian carbonates.

A possible inhibitor of aragonite is aqueous orthophosphate, PO_4^{3-}. There is evidence for elevated seawater phosphate levels from Neoproterozoic sediments [2], and evaporation of phosphate-bearing seawater results in sufficient carbonate supersaturation to precipitate amorphous calcium-magnesium carbonate. The retardation of crystal *growth* by phosphate has been well-characterised by pH-stat experiments [3], but few quantitative constraints exist on the mechanisms for the inhibition of aragonite and calcite *nucleation* by phosphate.

We precipitated calcite and aragonite from seawater-like solutions containing phosphate at concentrations of 0 to 16 µM. The induction time and growth rate were determined using timelapse photography, continuous pH measurements and solution sampling. Nucleation of aragonite and, to a lesser extent, calcite, was slowed above P_{tot} = 2 µM. In a series of experiments at constant initial supersaturation, the induction time increased exponentially with phosphate concentration, implying a linear increase in surface energy. We therefore propose a mechanism where phosphate adsorbs onto the surface of incipient aragonite nuclei according to the linear part of an adsorption isotherm, increasing interfacial energy and therefore the kinetic barrier to nucleation. This is comparable with the mechanism for the inhibition of calcite nucleation by Mg^{2+} in the modern oceans, and quantitatively constrains the environmental conditions necessary for abiotic non-classical crystallisation of carbonates.

[1] Strauss & Tosca (2020); *Geology* 48, 599–603.

[2] Roest-Ellis *et al.* (2023); *Geochemistry, Geophysics, Geosystems* 24.

[3] Burton & Walter (1990) *Geochimica et Cosmochimica Acta* 54, 797–808.