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Polymorph selection during crystallisation of amorphous precursors in seawater: experimentally modelling aspects of foraminiferal biomineralisation

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The biomineralisation process of organisms whose shells are used for climate reconstruction is a major source of uncertainty in confidently relating proxy signals to environmental conditions. This is especially relevant for foraminifers, a group of calcareous-shelled unicellular marine microplankton, as they provide one of the most important archives for paleoclimate reconstruction. It has been suggested that calcification in foraminifers proceeds via metastable precursors such as vaterite and/or amorphous $CaCO_3$ (ACC) [1,2], likely formed from endocytosed seawater subject to chemical alteration such as elevation of pH [3,4]. The properties of ACC precipitated from seawater, however, have only been sparsely investigated [5], and the crystallisation dynamics are unknown.

To investigate the inorganic driving forces at play, we reproduced calcification in an experimental seawater model system, by mimicking a process in which ACC is first formed and subsequently crystallised. We find that ACC made from seawater crystallises to calcite in seawaters with widely varying Mg/Ca and $[SO_4^{2-}]$, even if the respective solution composition would favour aragonite or vaterite if precipitation had occurred without the presence of a detectable ACC precursor.

These observations indicate that at solution conditions presumably relevant to foraminiferal biomineralisation, inorganic driving forces allow for the formation of calcite in normal seawater, via ACC, without the involvement of a biological control on the Mg and/or Ca concentration of the calcification site. Thus, our findings demonstrate that mineralogical control may be almost completely decoupled from solution composition at the site of crystallisation, if ACC is involved. This suggests that, if biological control over the chemistry of the calcification site occurs, it is not necessarily in order to direct shell polymorph selection, a conclusion that is not only relevant to foraminiferal calcification, but applies to marine biomineralisation in general.

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