

The role of Archaea in low temperature dolomite formation

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Pervasive in the ancient rock record, primary dolomite remains scarce in modern systems at low temperatures (< 50°C), even those systems supersaturated with respect to dolomite. This scarcity is attributed to kinetic inhibition of precipitation including ion complexation, hydration spheres and the presence of sulfate. No longer considered a purely geochemical problem, the impacts of live bacteria on the controls of dolomite formation have been extensively studied and disordered phases have been documented [1]. Recent work has demonstrated that methanogenic Archaea can also influence low temperature dolomite formation producing ordered, stoichiometric phases [2, 3].

Using both pure cultures and mixed consortia in controlled laboratory experiments we have demonstrated that Archaea uniquely influence dolomite precipitation at low temperature. Methanogenic Archaea impart stable isotopic signatures indicative of specific metabolisms and precipitates form from solutions slightly supersaturated with respect to dolomite and at Mg:Ca ratios ~1.

Utilizing other, non-methanogenic Archaea we demonstrate that, while often key in supersaturating conditions, metabolic activity is not necessary for dolomite formation and rather nucleation on the cell wall is the primary mechanism of precipitation (Figure 1). Our characterization of these Archaeal cell walls indicates that they are not only unique in their composition compared to bacterial cell walls but also possess distinctive surface functional group characteristics.

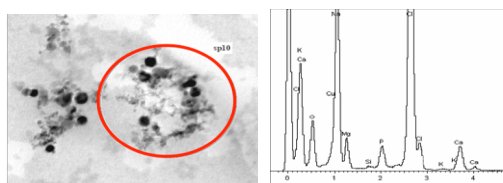


Figure 1: TEM (left) nano-crystals of dolomite forming on lysed cells of *H. sulfurofontis*. EDS (right) of circled area.

This evidence lends strong support for a role for Archaea in low temperature dolomite formation and identifies a key mechanism in the formation of ordered primary phases.

[1] Vasconcelos *et al.* (1995). *Nature* **377**, 220–222. [2] Roberts *et al.* (2004) *Geology* **32**, 277–280. [3] Kenward *et al.* (2009) *Geobiology* **7**, 556–565.

Boron isotopes in Southern Ocean deep sea corals

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Today the Southern Ocean is experiencing changes in carbonate chemistry with potential impacts on calcifying fauna. Similarly there were likely to have been large changes in pH in the past, associated with transient shifts in upwelling. Studying past changes in Southern Ocean carbonate chemistry, and its effect on calcifying organisms may help to better assess their fate in the light of anthropogenic ocean acidification.

Carbonate formed by marine organisms incorporates boron, and the speciation of boron and fractionation of its isotopes are sensitive to the pH of seawater. In order to test a new archive for past seawater pH we have analysed the boron chemistry of modern stylasterid corals collected from 130m to 2000m in the Drake Passage where there is a pH gradient with depth. Stylasterid corals have a global distribution and concentrically banded skeletons, but little is known about their growth rates or biomineralisation.

Boron concentrations range from ~60-160ppm and vary between species. The $\delta^{11}\text{B}$ values also show a large range, which again appear to be species dependent. Single species exhibit lighter values with decreasing pH (increasing water depth) similar to empirical calibrations of benthic foraminifera and theoretical predictions. The high boron concentrations provide the possibility of using these corals for ultra-high-resolution reconstruction of deep and high latitude pH in the past, but will require analyses of additional modern samples to confirm the pH-boron calibration.