The atomic-scale chemistry of a calcite bio-mineral interface

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Although numerous studies have revealed aspects of the physiology of biomineralization and architecture of biominerals [1], and inorganic crystal growth experiments have advanced our understanding of mineral precipitation in the context of biological systems [2], the structure and chemical composition of the mineralising interface between these two systems has remained elusive. Here, we use laser-pulsed Atom Probe Tomography (APT) to reveal the first atom-scale view of the interface between biomineral calcite and the Primary Organic Membrane (POM) in the 'test' of the planktic foraminifera *Orbulina universa*.

APT is a field-emission-source mass spectrometer, which measures the identity (mass/charge) and 3D position (to ~20 Å) of ions within a solid material. Recent developments have allowed its application to geological materials [3] [4], but the analysis of heterogeneous carbonate minerals has proved particularly challenging. Our data demonstrate the feasibility of the technique for analysing carbonate biominerals, and provide the most detailed chemically-resolved view of a calcite bio-mineral interface to date.

We find elevated Na and Mg concentrations within the POM relative to adjacent calcite, which are able to account for some of the puzzling internal trace-chemical heterogeneity patterns observed in foraminifera.

In the surface 2nm of the POM we observe a 4-10 fold increase in Na, peaking at 0.6 mol/mol Ca. This reveals that the POM surface exibits ion-specific recruitment during early biomineralisation.

Given this surface-specific Na enrichment, we offer a mechanistic hypothesis descibing ion recruitment and calcite templating by the POM, in context of the drive to reduce interfacial energy and minimise thermodynamic nucleation barriers [5], and well-documented (but poorly understood) ion-specific interactions with charged organic surfaces [5].

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