

Microstructural crystallography of foraminifer shells: implications for the biomineralisation pathway and response to diagenesis

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Mechanistically understanding foraminifer biomineralisation and fossilisation is vital knowledge for precise paleoclimate reconstructions using fossil shells, as well as predicting the resilience of the marine microorganism to ongoing ocean acidification. For this, a crucial aspect is detailed knowledge of the shell organisation on a crystallographic level. This allows for the identification of phase transformations and alteration processes both at formation and diagenesis, facilitating a fundamental relation to geochemical composition. To investigate the microstructure and crystallography of the shells, we have performed synchrotron-based high-resolution X-ray powder diffraction experiments on live-caught, core top, and fossil planktic foraminifer shells, and compared to calcite precipitated in seawater through (nonclassical) pathways. These reference calcites were prepared to imitate different aspects of foraminiferal biomineralisation processes: presence of organic matter, via slow precipitation or an amorphous CaCO_3 (ACC) precursor. By comparing in situ measurements of the crystallographic and microstructural response of these calcites during heating-and-quenching experiments, we find consistent and distinct patterns of changes in lattice parameters, peak shape, and micro strain. We propose that such patterns could serve as a proxy for the microstructure, and hence the formation pathway of biominerals. Different heat-induced changes may reflect different types of structural rearrangement, for example, through release of occluded organic matter or remnants of ACC. In the case of foraminifers, we find patterns consistent with both the release of organic matter and potential evidence for the presence of ACC in the biomineralisation pathway, along with indications for a substantial change in microstructure between live-caught and core top specimens. This information provides support for the model of an ACC-based, organic matter-mediated biomineralisation mechanism in foraminifers. Through fossilisation, we observe limited crystallographic change through a range of conditions, while clear microstructural changes are present in samples that express geochemical alteration – providing a tool to help address potential bias in paleoclimate