

## Mg incorporation modes in foraminifera: STXM of biogenic calcite

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The Mg/Ca ratio in calcite shells ('tests') of foraminifera is a widely-used empirical palaeoclimate ocean temperature proxy. We have tested the fundamental assumptions behind this proxy, and shed light on the mechanisms underpinning this vital oceanographic tool by exploring the distribution and local chemical environment of Mg in foraminifera using STXM and NEXAFS techniques at the ALS synchrotron.

Throughout the development of the Mg/Ca proxy, it has been tacitly assumed that Mg in foraminifera tests substitutes directly into the calcite lattice[1]. This assumption is based on XRD analyses of various high-Mg biogenic carbonates, where Mg incorporation causes shifts in position of Bragg diffraction peaks [2,3]. The extrapolation of this trend to foraminiferal calcite conveniently links the proxy to inorganic precipitation experiments, and provides a theoretical mechanistic framework to understand it. However, the concentrations of Mg in most foraminifera are too low (<1 mol%) to conclusively test this hypothesis using XRD methods. Attempts to apply these methods to foraminifera have revealed trends in peak position and shape with depth and Mg content, and appear to show a system composed of two distinct calcite phases[4,5]. Electron microprobe [6-8], LA-ICP-MS [9] and high-resolution nanoSIMS mapping (Sadekov, pers. comm.) of foraminifera tests have revealed the presence of high-'impurity' bands oriented parallel to the test surface, enriched in Mg, Sr, S, organic molecules and other impurities. While this supports the two-phase model proposed in XRD studies, it precludes the inference of Mg as the sole cause of the peak shifts observed in the two-phase system, which could be attributable to one or many of the impurities concentrated in these bands.

The banding of Mg and its coincidence with other impurities emphasises a key question highlighted by Dodd [1] when the proxy was still in its infancy: how is Mg incorporated into mineral skeletons? By direct substitution into the calcite lattice, interstitially into a separate distinct mineral phase, adsorbed onto mineral surfaces, or associated with organic compounds? We have addressed this fundamental question using the STXM and NEXAFS capabilities of ALS beamline 11.0.2 to examine the distribution and local environment of Mg in two contrasting species of foraminifera.

Our data conclusively demonstrate that the Mg in both high- and low-impurity bands is incorporated in the same mode, and is characterised by Mg K-edge spectra that are most similar to that of dolomite, where Ca and Mg are interchangeable and present in octahedral coordination. These data show conclusively that Mg is ideally substituted into foraminiferal calcite, validating the assumptions underlying the use of the Mg/Ca proxy. The origin of Mg heterogeneity remains an open question, and TEM studies are underway to investigate microstructural variations in Mg heterogeneity.

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