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The coordination of Mg in foraminiferal calcite

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ABSTRACT

The Mg/Ca ratio of foraminiferal calcite is a widely accepted and applied empirical proxy for ocean temperature. The analysis of foraminifera preserved in ocean sediments has been instrumental in developing our understanding of global climate, but the mechanisms behind the proxy are largely unknown. Analogies have been drawn to the inorganic precipitation of calcite, where the endothermic substitution of Mg for Ca is favoured at higher temperatures. However, evidence suggests that foraminiferal Mg incorporation may be more complex: foraminiferal magnesium is highly heterogeneous at the sub-micron scale, and high Mg areas coincide with elevated concentrations of organic molecules, Na, S and other trace elements. Fundamentally, the incorporation mode of Mg in foraminifera is unknown. Here we show that Mg is uniformly substituted for Ca within the calcite mineral lattice. The consistency of Mg-specific X-ray spectra gathered from nano-scale regions across the shell ('test') reveals that the coordination of Mg is uniform. The similarity of these spectra to that produced by dolomite shows that Mg is present in an octahedral coordination, ideally substituted for Ca in a calcite crystal structure. This demonstrates that Mg is heterogeneous in concentration, but not in structure. The degree of this uniformity implies the action of a continuous Mg incorporation mechanism, and therefore calcification mechanism, across these compositional bands in foraminifera. This constitutes a fundamental step towards a mechanistic understanding of foraminiferal calcification processes and the incorporation of calcite-bound palaeoenvironment proxies, such as Mg.

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1. Introduction

The Mg/Ca ratio of foraminiferal calcite is a widely accepted and applied empirical proxy for ocean temperature (Bohaty et al., 2012; Elderfield and Ganssen, 2000; Garidel-thoron et al., 2005; Lea et al., 2000; Nürnberg et al., 2000). The construction of Mg/Ca records from foraminifera preserved in ocean sediments has been instrumental in developing our understanding of global climate, but the mechanisms behind the proxy have remained largely unknown. Use and interpretation of the Mg/Ca palaeothermometer is based on the assumption that Mg is inorganically hosted in the calcite mineral lattice, but foraminiferal Mg/Ca ratios differ significantly from those derived from inorganic precipitation experiments (Bohaty et al., 2012; Elderfield and Ganssen, 2000; Garidel-thoron et al., 2005; Lea et al., 1999, 2000; Morse and Bender, 1990; Nürnberg et al., 2000). Most foraminifera contain orders of magnitude less Mg (Morse and Bender, 1990), Mg in foraminiferal calcite is around three times more sensitive (up to ~10% per °C) to temperature change (Lea et al., 1999), and both Mg concentration and temperature sensitivity show high inter- (Morse and Bender, 1990) and intra-species (Elderfield et al., 2002) variability between organisms inhabiting similar environments (Hintz et al., 2006; Kısakürek et al., 2008; Lea et al., 1999; Russell et al., 2004). These disparities are labelled 'vital effects' (Urey et al., 1951; Weiner and Dove, 2003), and are broadly attributed to biological mechanisms that influence the calcification process. As long as the offsets caused by 'vital effects' are systematic, and remain consistent within species, they can be overcome by robust calibration studies (Anand et al., 2003; Elderfield et al., 2006; Nürnberg et al., 1996), and do not represent an insurmountable barrier to the application of the palaeothermometer. However, evidence suggests that foraminiferal Mg incorporation may be more complex: foraminiferal Mg is highly heterogeneous at the sub-micron scale (Eggins et al., 2004; Erez, 2003; Kunioka et al., 2006; Sadekov et al., 2005), and high Mg areas coincide with elevated concentrations of organic molecules, Na, S and other trace elements (Erez, 2003; Kunioka et al., 2006). Internal heterogeneity is both diverse, with different species exhibiting either systematic

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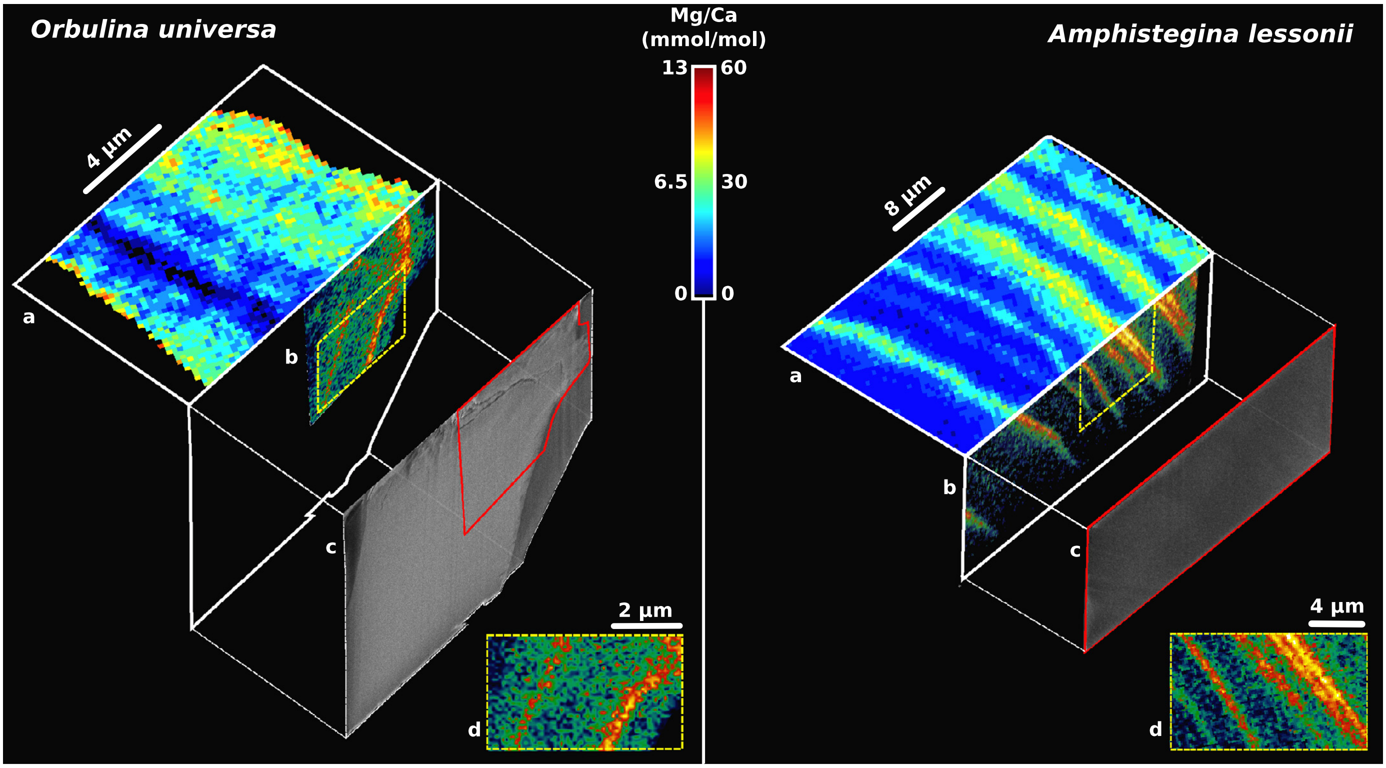

Fig. 1. The distribution of Mg in foraminifera. Electron microprobe maps of the samples reveal patterns of Mg/Ca banding (A), which are in agreement with Scanning Transmission X-ray Microscope (STXM) images of Mg-Specific X-ray absorption (B, arbitrary units) in the thin-section samples (C). This confirms that the STXM Mg signal is real, and not an artefact of sample density or thickness variations. This is evident in the uniformity of the off-peak STXM Optical Density (OD) images of the thin section samples (C). In (C) brightness is a function of absorbed photons, and the dark areas either side of the *Orbulina* specimen are sections of the resin used to mount the samples. Magnified areas of the STXM images denoted by dashed yellow boxes show the length scale of Mg heterogeneity to be in the order of 1–300 nm (D). The Mg bands in the *Amphistegina* specimen (B and D) taper towards the bottom of the image. This reflects a decrease in sample thickness, not a reduction in Mg content. The *Amphistegina* (B) image was taking in transmission mode (25 nm Zone Plate, 150 nm step, 2 ms dwell), and the *Orbulina* (B) image in fluorescence mode (40 nm Zone Plate, 100 nm step, 50 ms dwell). The colour scale bar denotes Mg/Ca in the electron microprobe maps (A), and the STXM images are in arbitrary units.

banding (Fig. 1) or apparently random variations (Sadekov et al., 2005), and large, with [Mg] varying by up to a factor of 10 across the test. The coincidence of Mg enrichment with high concentrations of other trace elements and organic molecules (Erez, 2003; Kunioka et al., 2006) raises the possibility that Mg is incorporated in association with these other components, rather than directly substituted for Ca. If Mg exists in association with organics, Na or S, or in a coordination other than ideally substituted into calcite, the connections drawn between modern and fossil species by the application of empirical calibrations must be questioned. Furthermore, if the coordination of Mg differs between the high-Mg ('on-band') and low-Mg ('off-band') regions, this would imply a complex two-phase incorporation mechanism, which would invalidate the inorganic precipitation analogies. The small size (typically <500 μm Ø, walls 5–50 μm thick) and high purity (>99% $CaCO_3$) of foraminifera has thus far precluded the direct mineralogical investigation of foraminiferal Mg. Here we apply nano-scale synchrotron X-ray spectroscopy techniques to address the fundamental uncertainties raised by internal Mg/Ca heterogeneity, by conducting a nano-scale mineralogical investigation of the atomic coordination of Mg in on- and off-band regions through the foraminiferal test.

2. Methodology

We characterise the coordination of Mg in two disparate species of symbiont-bearing foraminifera using Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. Both the benthic *Amphistegina lessonii* (∼40 mmol/mol Mg/Ca) and the planktic *Orbulina universa* (1–10 mmol/mol Mg/Ca) are known to exhibit systematic Mg banding (Eggins et al., 2004; Erez, 2003; Kunioka et al., 2006; Sadekov et al., 2005), which was confirmed in our specimens by electron microprobe maps (Fig. 1A). Test cross-sections were prepared using a focused ion beam (FIB, Fig. 1C), and analysed using a scanning transmission X-ray microscope (STXM, Fig. 1B and D).

2.1. Sample preparation

Recently alive specimens of *Orbulina universa* and *Amphistegina lessonii*. were obtained from plankton tow samples and cultures, respectively. Individual tests were broken into several pieces with a fine scalpel blade in ethanol, and the fragments mounted on double-sided tape with the flattest broken edge in plane with the tape surface (so the majority of the fragment protruded normal to the tape surface). These mounted fragments were set in epoxy resin following a standard procedure for preparing petrographic samples. The set resin blocks were cleaned with petroleum ether to remove traces of the tape adhesive, and polished to expose the edges of the test fragments. The polished surface was carbon coated, and imaged in an SEM to guide the location of the sample fragments in a focused ion beam (FIB) instrument.

Sections were cut bisecting the test wall perpendicular to the polished surface in a Helios NanoLab FIB, following a modification of FEI™'s standard procedure for producing and extracting TEM samples (Reyntjens, 2006). Deviations from the normal methods were necessary because the foraminifera sections were wedge shaped, and larger and thicker than normal TEM sections. Wedge-shaped samples were required to allow for uncertainties in the required sample thickness for STXM analysis.

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