The distribution and coordination of trace elements in *Krithe* ostracods and their implications for paleothermometry

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Abstract

The Mg and Sr content of ostracod valves have been used to reconstruct past temperature and salinity, and their stable isotopes have been used to reveal aspects of marine, lake and estuary hydrology. However, significant uncertainties surround ostracod calcification processes, the incorporation mechanisms of trace elements, and the sensitivity of proxy tracers to complex confounding factors. The valves of most ostracods are composed of micron-scale crystalline grains embedded in an organic matrix. The fine-scale geochemistry of these structures, and the nature of the influence of biological mineralisation processes on valve chemistry, remain poorly constrained. We have performed sub-micron resolution X-ray microscopy of a marine *Krithe* ostracod valve, and determined the chemical coordination of Mg, and the distribution of Mg, Na and S throughout the crystal-organic valve structure. These trace elements display systematic sub-micron-scale compositional variations within the mineral grains and inter-granular matrix of the valve ultrastructure. These patterns imply that *Krithe* biomineralisation processes significantly modulate trace element incorporation at the sub-micron scale. Thus *Krithe* chemical composition is likely to be decoupled to some extent from the water in which they calcified. Most importantly, Mg K-edge Near-Edge X-Ray Absorption Fine Structure (NEXAFS) spectra, and the coincidence of high-Mg regions with S-rich organic layers reveal that Mg is not primarily hosted in the calcite structure in the valve. Our results highlight the need to understand the processes that drive this fine-scale chemical heterogeneity and their influence on connections between the external environment and valve geochemistry, if ostracods are to be used as sources of paleoenvironmental proxies.

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1. INTRODUCTION

Carbonate biominerals provide an unparalleled geochemical archive of Earth’s climate, which has been instrumental in understanding climate cycles and feedbacks (Lea, 2014). The use and interpretation of paleoenvironmental proxies depends upon robust relationships between biomineral geochemistry and external environmental conditions. These relationships are based upon the physical and chemical processes governing the distribution and speciation of elements in seawater, and the incorporation of these elements into carbonate minerals, which predict connections between the environment and shell geochemistry that can be demonstrated in inorganic precipitation experiments (e.g. Mucci and Morse, 1983). However, biomineralisation processes often cause deviations from behaviour predicted...
by inorganic experiments (Weiner and Dove, 2003), so these geochemical proxies must rely on empirical, species-specific calibrations to account for these discrepancies (e.g. Anand et al., 2003). The interpretation of paleoproxies includes the implicit assumption that the tracers are incorporated directly into the mineral structure. This assumption has been shown to be true for Mg and B in foraminifera (Branson et al., 2015, 2013; Yoshimura et al., 2015), and Mg in brachiopods (Cusack et al., 2008; Yoshimura et al., 2015), bivalves, and calcitic corals (Yoshimura et al., 2015). In contrast, Mg in aragonitic corals appears to be hosted in a disordered, non-crystalline, and likely organic phase (Finch, 2008). If a trace element is hosted within the mineral lattice, knowledge of inorganic mineral systems may be used to understand the physical factors affecting its incorporation and subsequent preservation. Conversely, if an element is hosted in an alternative mineral or organic phase, other factors may control the incorporation and preservation of the tracer, and paleoproxy records derived from it may be harder to interpret.

The stable isotopic composition and trace element content of the bi-valved, calcitic carapace (outer shell) of marine, estuarine, and lacustrine ostracods have been developed and applied as paleoenvironmental tracers (Chivas et al., 1991a, 1986b, 1983; Cronin et al., 2005, 2000; De Deckker et al., 1988; De Deckker and Forester, 1988; Dwyer et al., 2002; Elmore et al., 2012; Gray et al., 2014; Horne et al., 2012; Wansard and Mezquita, 2001). The Mg/Ca and Sr/Ca of ostracod valves are used as paleotemperature and paleosalinity proxies (Chivas et al., 1986b, 1983). However, variations in ostracod Mg/Ca and Sr/Ca often deviate from relationships established in both inorganic precipitates and other biominerals (Elmore et al., 2012; Ito et al., 2003; Ito and Forester, 2008). The likely cause of such discrepancies are the poorly understood mechanisms of ostracod calcification (Ito and Forester, 2008).

Crustaceans mineralise their cuticle via a series of complex steps, involving epidermal layers, chitinous frameworks, and organic-rich gel layers (Yamada et al., 2005). In many crustaceans, the main carbonate component of in-vivo cuticle is amorphous calcium carbonate (ACC; Becker et al., 2005; Raz et al., 2002). This may also be the case in ostracods, given observations of valve ultrastructure, which reveal granular carbonate structures enclosed within an organic framework (Jorgensen, 1970; Keyser and Walter, 2004; De Deckker, 2017) homologous to other crustaceans. The involvement of ACC in crystallisation is known to influence calcite trace element content in inorganic systems (Wang et al., 2009), and could alter the sensitivity of trace element uptake to environmental parameters, particularly given the observation of ACC formation via calcium phosphate precursors (Keyser and Walter, 2004). Given the complex ultrastructure of ostracod valves, trace elements may be incorporated directly into the mineral structure or the organic chitinous framework, or be excluded to interstitial microdomains between the mineral and organic components, or a mixture of all three. Each trace element incorporation pathway may exhibit a distinct response to external environmental variability, and would require a distinct interpretation of trace element paleoenvironmental proxies.

Here, we investigate the sub-micron scale distribution and coordination (chemical bonding environment) of S, Mg and Na within the carapace of a *Krithe* ostracod using an X-ray Photo-Emission Electron Microscope (XPEEM). The coordination and distribution of S allows us to map organic material within the *Krithe* carapace. The coordination and distribution of Mg reveals aspects of Mg incorporation that shed light on the utility of the ostracod Mg/Ca temperature proxy. Finally, while the function of Na in ostracod mineralisation is unknown, it offers the potential to examine the similarity of incorporation of different ions into the carapace by comparison to the distribution of Mg, allowing us to probe the cation-specificity of trace element incorporation into the carapace. Together, the distributions of these elements reveal the significant influence that *Krithe* biomineralisation processes exert on sub-micron-scale geochemistry.

2. METHODS

2.1. Sample preparation

Specimens of benthic marine *Krithe* ostracods were obtained from the top 5 cm of deep-sea sediment core KN166-14 11JPC from the Gardar Drift (2707 m water depth; Iceland Basin, NE Atlantic), well above the lysocline (~4000 m). The top of core KN166-14 11JPC was shown in a previous study to be of Late Holocene age (665 ± 5 Calendaryears ago) using AMS 14C dating (Elmore and Wright, 2011; Elmore et al., 2015). For our sample preparation, ~5 cc of sediment was washed through a 63 μm sieve using deionised water and then dried over night at 40 °C. The carapace was brushed clean to remove observable surficial particles and visually inspected to ensure good preservation (translucent, non-granular appearance). The environmental conditions that the carapace was formed in are not well constrained.

An individual carapace valve was mounted in degassed EpoFix resin, and the sample surface was polished to a colloidal silica finish (1–5 nm grains). Polished samples received a two-step carbon coating: protective windows were placed over the specimens, and a ~50 nm carbon coat was applied to the exposed resin surface, the windows were then removed and a 1–2 nm carbon coat was applied to coat the entire sample surface.

A specimen of the benthic foraminifera *Aphistergina lessontii*, obtained from a live stock culture at Cambridge University, was also prepared following the same method. This sample serves as a coordination reference for Mg, which has previously been determined to be in an octahedral coordination, substituted for Ca in the calcite structure (Branson et al., 2013).

Microfossil samples were mounted in proprietary holders, designed to secure the specimen and provide a conductive path across the sample surface, and analysed by XPEEM at beamline UE49 of the BESSY II synchrotron.
using ImageJ (Schindelin et al., 2012), normalised between zero and one, and scaled by aligning the inflection points in the off-peak profile to account for differences in grain size.

2.4. Electron probe maps

Electron probe micro-analysis (EPMA) maps of the specimens were collected after XPEEM analyses using a modified technique after Sadekov and Eggins, 2005, employing a finer beam (~1 μm Φ), a smaller step size (0.5 μm), and a 1 s count time for all analytes.

2.5. Scanning electron microscopy

SEM images were taken using a Hitachi TM 3000 microscope in both normal imaging mode, and topographic imaging mode, which increases topographic contrast by comparing left- and right-illuminated images.

3. RESULTS

3.1. Broad-scale sample structure

SEM imaging revealed heterogeneities in electron density on the sample surface (Fig. 1B), consistent with a cross-sectional view of the crystal-organic matrix structure present within *Krithe* valves (De Deckker, 2017). These features do not correspond to sample topography, which was negligible on the scale of our analyses (Fig. 1B). EPMA maps of Mg/Ca and Na/Ca reveal that both elements are relatively homogeneous at the micron-scale (Fig. 1C), and certainly compared to the systematic chemical heterogeneity observed in other biominerals, including foraminiferal calcite (Branson et al., 2013; Sadekov and Eggins, 2005). There is some heterogeneity in both Mg and Na at the ~10 μm scale, with a ~5 μm wide band of elevated Mg and Na concentration running parallel to the outer valve surface, in rough agreement with a similar high Mg/Ca band observed in De Deckker’s (2017) microprobe study (Fig. 1C). There is also a marked increase in Na and especially Mg in the muscle scar, which is likely to be enriched in organic material (Fig. 1C).

An XPEEM off-edge total electron yield (at an energy that does not correspond to a specific elemental absorption edge) image shows the electron density at the sample surface at sub-micron-scale resolution (Fig. 2). This reveals a distinctive ‘granular’ pattern, with lower-electron-density grains between 0.5–2 μm long embedded in a higher-density matrix, reminiscent of early ostracod TEM micrographs (Jørgensen, 1970), and again consistent with the crystal-organic matrix structure of the *Krithe* valve (De Deckker, 2017). Based on comparison to these previous ultrastructural observations, the ‘bright’ regions likely correspond to relatively electron-dense organic materials, and the ‘dark’ regions to relatively electron sparse crystalline material. The specimen surface is flat on the scale of these features, and therefore they are not artefacts of sample topography (Fig. 1B). Spectral data are presented from the entire sample (‘total’), electron-dense (‘bright’) and electron-sparse (‘dark’) regions separately, to investigate...
3.2. Spectral results

The Mg spectra measured from foraminiferal calcite contains the same spectral features as those collected by previously-reported scanning transmission X-ray microscopy (STXM) NEXAFS techniques (Fig. 3) (Branson et al., 2013; Yoshimura et al., 2015). The energy resolution of the XPEEM is lower than the X-ray absorption or fluorescence techniques employed in our previous studies, but the similarity of our foraminiferal spectrum to previous results demonstrates that the XPEEM is able to resolve the coordination of calcite-bound trace elements of similar concentration to Mg in *A. lessonii*. The bulk Mg/Ca of *Krithe* is typically 8–17 mmol/mol (Elmore et al., 2012; Gray et al., 2014; Mewes et al., 2015), compared to 10–40 mmol/mol in *A. lessonii* (Branson et al., 2013). Any Mg spectra from *Krithe* may be up to 5x less intense than *A. lessonii*, but this comparison serves to demonstrate the accuracy of the Mg edge position in XPEEM, and the overall shape of calcite-hosted Mg spectra.

The Mg absorption edge in the ostracod specimen is broad, lacks distinct features. The absorption edge position, and the overall Mg spectra shape is dissimilar from the foraminiferal Mg spectrum (Fig. 3). The *Krithe* Mg spectrum also bears no clear similarity to any of the wide variety of previously measured spectra of Mg-bearing mineral phases (Branson et al., 2013; Cusack et al., 2008; Farges et al., 2009; Finch, 2008, 2007; Foster et al., 2008; Yoshimura et al., 2015), which tend to be characterised by well-defined peaks. The Mg spectra from ‘bright’ and ‘dark’ sample regions are of different intensities, but there are no consistent differences in their shape, indicating that while ultrastructural changes in the carapace correspond to changes in Mg concentration, there is no variation in Mg coordination.

As with the *Krithe* Mg spectrum, the S spectrum is broad, and lacks well-defined features (Fig. 4A). Two broad peaks at ~150 and ~160 eV appear to varying degrees in the ostracod S spectra. The ~160 eV peak is most intense in the ‘bright’ regions of the valve, and dominates the ‘total’ spectrum. This peak is consistent with the S L$_{2,3}$-edge, although the overall peak structure is distinct from previously published S spectra (Fleet, 2005; Kasrai et al., 1990; Pingitore et al., 1995). The ~150 eV peak dominates in the ‘dark’ regions, and is a minor component in the ‘total’ and ‘bright’ regions. This could imply a significant change in S coordination between the grains and the inter-grain matrix, although a 10 eV shift is large and improbable. Alternatively, the ~150 eV peak could be attributable to...
the L₂-edge of Phosphorous (e.g. Yang et al., 2012), which would imply a concentration of P in the ‘dark’ (crystalline) region.

The Krithe Na spectrum is noisy because of the relatively low Na concentration, the low quantum yield of the Na K-edge, and limits on instrument count time. This precludes any conclusive identification of peaks within the data. However, smoothed spectra show a double-peaked structure at the Na edge (Fig. 4B), which bears no resemblance to any Na mineral spectra presently reported in the literature (De Wispelaere et al., 2004; Neuville et al., 2004; Yoshimura et al., 2017). Meaningful conclusions on the Na coordination state cannot be drawn on the basis of these spectra, but they do confirm the position of the Na K-edge in the ostracod specimen, allowing the creation of Na maps.

As with the Mg spectrum, there are no significant Na spectral differences between ‘bright’ and ‘dark’ regions of the Krithe ultrastructure.

3.3. Elemental distribution

Absorption-edge maps of Mg, Na and S within the Krithe valve (Fig. 2) all show distinctive patterns that correspond to aspects of the granular ultrastructure seen in the off-peak electron density image. These patterns are highlighted in cross-grain chemical profiles (Fig. 5). Both Mg and Na exhibit systematic heterogeneity within the low-density grains. Mg is elevated on the upper right of each grain, and depleted on the lower left, while Na shows the opposite pattern (Figs. 2 and 3). Maximum Mg intensities...
are observed in the inter-grain matrix, while maximum Na is observed within lower right edges of the grains. In contrast, S appears relatively homogenous and depleted within the grain body, and is enriched in the inter-grain matrix. Note that these absorption-edge maps are sensitive to both changes in element concentration and coordination. Thus, Mg and Na maps may be interpreted as elemental concentration maps because of their spatially homogeneous spectra, while the S maps are complicated by possible coordination changes, evident in the variation of S spectra between ‘bright’ and ‘dark’ regions.

4. DISCUSSION

Our XPEEM analyses corroborate the well-documented organic-mineral composite valve ultrastructure observed in previous studies of ostracods (Jørgensen, 1970; Keyser and Walter, 2004; De Deckker, 2017), revealing a network of mineral grains hosted within an organic matrix. Our elemental maps show systematic patterns of element distribution and coordination within the crystal grains and inter-crystalline organic matrix, which are present throughout the region of the valve analysed. Combined with the ubiquity of this crystal-organic structure within Krithe valves (De Deckker, 2017), these systematic patterns are likely to be characteristic of these structural units, and present throughout the entire valve. Our observations show that biomineralisation processes exert a significant, systematic influence on the sub-micron-scale chemistry of the valve, but we cannot discern how changes in the external environment or ontogeny may influence these patterns. The specific magnitudes and nature of the patterns observed in this study may be unique to this specimen, and considerable further ultrastructural work is required to investigate...
The role of these fine-scale processes play in modulating links between bulk valve chemistry and the external environment, and their use as paleoproxy recorders. Nevertheless, our ultrastructural chemical data provide an opportunity to investigate the contribution of specific aspects of ostracod biomineralisation to valve chemistry.

The broad S-edge spectrum in *Krithe* is indicative of a relatively disordered coordination environment, most likely associated with organic molecules. The high concentration and distinct coordination state of S within the electron-dense (‘bright’), inter-granular matrix may imply the presence of an interstitial sulphated organic molecule. For example, sulphated polysaccharides are common in numerous invertebrate calcareous structures, and are thought to play a role in facilitating ACC-mediated mineralization (Cuif et al., 2008), which is known to be important in ostracods (Keyser and Walter, 2004) and other crustaceans (Becker et al., 2005; Raz et al., 2002). The dominance of the 150 eV peak in the crystal grain (‘dark’) spectra may indicate a concentration of P within the crystal grains, which is consistent with previous observations of calcium phosphate precursors in ostracod mineralisation (Keyser and Walter, 2004).

The lack of similarity between our *Krithe* Mg spectra and the spectra of calcite-hosted Mg (Fig. 3) (Branson et al., 2013; Cusack et al., 2008; Farges et al., 2009; Finch, 2008, 2007; Foster et al., 2008; Yoshimura et al., 2015) suggests that the bulk of the Mg in the ostracod carapace is unlikely to be substituted for Ca in the calcite mineral structure. While determination of precise Mg coordination is not possible from our spectra, the broad nature of the Mg-edge implies a highly variable coordination state, most similar to that of organic-associated Mg that has been measured in previous studies (Branson et al., 2013; Finch, 2008, Yoshimura et al., 2015). Alongside the relatively high abundance of Mg within the S-rich, electron-dense matrix, and the relatively high Mg content of the non-soluble organic matrix of ostracods (Chivas et al., 1983), this implies that a significant portion of total valve Mg is hosted within the inter-granular organic matrix. The similarity of the Mg spectra between electron-dense matrix and electron-sparse grains further implies that even Mg present in the crystalline component of the valve may be hosted within intra-crystalline organic components.

The homogeneity of Mg and Na spectra throughout the valve ultrastructure allow us to interpret their absorption-edge maps as indicative of elemental concentration, rather than coordination changes. The relative distributions of Mg and Na offer insights into the mineralisation of crystal grains in the carapace. Within each grain, Na is more variable. Mg and S are both elevated within the inter-granular material, compared to the grain body. Na is most abundant within the grain body, on the left hand side. Thick lines and error envelope denote the mean and standard deviation of five profiles, extracted from the lines shown in Fig. 2. All profiles are normalised between zero and one, and are presented on an arbitrary, unitless scale.

![Cross-granular profiles reveal systematic compositional patterns within the carapace structure.](image)

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observations (Jorgensen, 1970; Keyser and Walter, 2004; De Deckker, 2017), but the implications for carapace geochemistry have thus far remained unexplored.

Based on our observations, it is clear that the processes of ostracod biomineralisation exert a strong influence over carapace chemistry. Understanding these controls, and their sensitivity to the external environment and ontogeny, is crucial to their use as a source of geochemical proxy material. Most importantly, our *Krithe* data show that Mg is not predominantly hosted within the calcite mineral lattice. This suggests that thermodynamic controls need not define the relationship between temperature and ostracod Mg/Ca. This raises two significant areas of uncertainty, which must be addressed if ostracods are to continue to be used as a source of paleoceanographic proxies:

1. *The controls on Mg uptake into organic material*. In particular, the relation of Mg uptake to temperature, and other environmentally variable factors (e.g. food supply, growth rate, salinity). Because of its high Mg content, the processes controlling organic chemistry have the potential to dwarf any thermodynamically-driven mineral-hosted Mg/Ca signal.

2. *The influence of diagenesis on valve organic content and composition*. The preservation of organic material is unlikely to be similar to calcite. This raises significant issues for the down-core application of ostracod Mg/Ca paleothermometer, as the rates of change of the composition and abundance of organic and mineral material with time are unknown.

It is possible that estuarine and lacustrine ostracod species may incorporate Mg using distinct mechanisms from the benthic marine *Krithe* ostracod investigated here, and could have predominantly calcite-hosted Mg. However, given the Mg-rich organic present in non-marine ostracods (Chave, 1954), and the similar organic-mineral composite structure of numerous ostracod species (De Deckker, 2017), we consider this unlikely. Whilst we are unable to address the coordination of Sr in this experiment, our results raise significant questions surrounding the incorporation mechanisms of all trace elements in ostracods. These must be addressed before the they can be confidently used as a source of geochemical paleoceanographic proxy material.

5. CONCLUSIONS

Our results indicate that the incorporation of Mg, Na, and S in *Krithe* are significantly modulated by biomineralisation processes at the sub-micron scale, and is not comparable to inorganic calcite precipitation. Therefore, the assumptions that normally underpin our use of calcite-bound paleoproxies cannot be applied to ostracods. Significantly, we find that Mg is not predominantly hosted in the *Krithe* calcite mineral lattice, and is concentrated in the inter-granular organic material within the carapace, which raises significant questions surrounding the mechanisms behind the Mg/Ca ostracod paleothermometer. Importantly, while we have revealed biomineralisation-driven patterns in valve chemistry, the specific patterns observed in this specimen may vary with external environment, ontogeny, or between species. The role of the selected micron-scale biomineralisation processes on modulating whole-valve geochemistry must be systematically evaluated, if their trace elements are to be used as a source of paleoproxy material.

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