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XANES determination of magnesium speciation in shells of two marine bivalve molluscs

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Recent studies have demonstrated generally weak relationships between seawater temperature and Mg/Ca ratios in calcite marine bivalve mollusc shells, despite an expected thermodynamic control on Mg incorporation. Several studies have suggested that such weak relationships could be due to Mg being non-lattice bound and associated with the shell organic matrix. In this study we use XANES to investigate the structural state of Mg in the shells of two species of marine bivalve mollusc, Mytilus edulis and Pecten maximus. Both species of mollusc were cultured in laboratory constant-temperature aquaria. Mg K-edge XANES analyses were completed using the LUCIA beamline, then situated at the Swiss Light Source. Initially, Mg and S (as a proxy for the sulphated organic matrix) distributions were mapped using Synchrotron XRF within the new shell growth laid down during the culturing period. Subsequently, XANES were collected for different pixels within the maps that had contrasting Mg and S distributions. XANES spectra are consistent within the Pecten maximus shell, despite previous studies that have shown a marked heterogeneity of Mg/Ca ratios within this species, and are indicative of Mg being hosted in a calcite-type phase. In contrast, XANES of Mytilus edulis indicates that Mg is hosted predominantly in an organic-type phase. A simple two component numerical modelling will allow an assessment of the proportions of calcite and organic Mg hosts in the two species. Speciation studies using XANES thus indicate that Mg is hosted in different phases in the two marine bivalve mollusc species investigated in this study; such an observation clearly has implications for the application of Mg/Ca thermometry in these calcifying organisms.