



Microscale magnesium distribution in shell of the Mediterranean mussel *Mytilus galloprovincialis*: An example of multiple factors controlling Mg/Ca in biogenic calcite

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ABSTRACT

Since magnesium concentration (Mg/Ca) in biogenic calcite is considered to reflect water temperature during precipitation, the magnesium-to-calcium ratio has been examined as a proxy for water temperature in paleoclimate research, although factors other than temperature may also influence Mg/Ca in biogenic calcite, thereby introducing a potential bias in the relationship between Mg/Ca and temperature observed in inorganic systems. To better understand factors controlling Mg incorporation into the calcitic shells of bivalves, the distribution of Mg in the Mediterranean mussel *Mytilus galloprovincialis* was studied, being compared with ambient sea surface temperature (SST), shell growth rate and the distribution of organic matter. Although a positive relationship between Mg/Ca and SST was observed, Mg/Ca had been influenced by additional factors, including the enhancement of Mg incorporation by organic matter, evidenced by the growth line being more Mg-enriched than the growth increments. Furthermore, Mg/Ca was relatively enriched in the undulating (higher curvature) shell portion, being linked to neither SST, growth rate or organic matter. Zoning of Mg²⁺/Ca²⁺ within extrapallial fluid at the time of undulating shell portion formation was hypothesized, and heterogeneous Mg distribution in contemporaneously formed shell portions concluded as limiting the usability of *Mytilus* shell Mg/Ca as a proxy for water temperature.

1. Introduction

Shells of bivalve mollusks consist of calcium carbonate crystals and intra- and inter-crystalline organic material, the rate of shell formation being reflected in periodic growth patterns, represented by a combination of growth increments (fast growth) and growth lines (slow growth), the latter being relatively enriched with organic macromolecules (Lutz and Rhoads, 1980). Shell growth patterns (lunar, daily, fortnightly and annual cycles, e.g. Kubota et al., 2017; Schöne and Surge, 2012; Tanabe et al., 2017) provide a means for placing each shell portion into a precise temporal context, changes in trace and minor elemental composition (e.g. Mg/Ca), and isotope data (e.g. δ¹⁸O) along the growth direction reflecting environmental variability (Klein et al., 1996; Schöne, 2013; Schöne and Krause, 2016). Thus, the combined

analyses of growth patterns and chemical composition enable the reconstruction of past environmental changes with high temporal resolution.

In particular, Mg/Ca of calcitic bivalve shells has been proposed as a proxy for water temperature (Klein et al., 1996), the temperature dependency of Mg/Ca having been demonstrated by inorganic precipitation of calcite at different temperatures (Oomori et al., 1987) and therefore used to justify the former proposal. On the other hand, laboratory experiments and geochemical modeling, which addressed Mg incorporation from aqueous solution into calcite (Mavromatis et al., 2013, 2017; Paquette and Reeder, 1995; Stephenson et al., 2008; Sun et al., 2015; Wang et al., 2009), demonstrated that such is influenced by multiple, sometimes interacting factors (other than water temperature), including the growth rate of calcite (Mavromatis et al., 2013), crystal

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