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An examination of potential controls on shell Mn/Ca ratios in the calcite of the bivalve *Mytilus edulis*

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The Mn/Ca ratios in the calcite of marine bivalves have been suggested to reflect both the dissolved and/or particulate Mn concentrations of seawater. However, a clear understanding of what controls shell Mn/Ca ratios is still lacking and a clear quantitative relationship between dissolved and/or particulate Mn and shell Mn/Ca ratios in either calcitic or aragonitic molluscs must be established and validated before any application of a bivalve Mn/Ca palaeoproxy. To study the influence of seawater dissolved and particulate Mn concentrations on bivalve shell calcite Mn/Ca ratios, *Mytilus edulis* specimens were grown in a field experiment in the Menai Strait, U.K., for a one-year period. A single maximum (0.54 μM) during spring dominated the annual variation of seawater dissolved Mn concentrations, while seawater particulate Mn concentration was highest (up to 0.18 μM) during autumn and winter, although smaller increases in particulate Mn during the phytoplankton spring bloom were also observed. In *M. edulis*, shell Mn/Ca ratios of newly precipitated calcite showed a double-peak annual variation with maximum values (up to 0.19 mmol/mol) during early spring and early summer. None of the two maximum of shell Mn/Ca ratios can be explained by an increase in either seawater dissolved or particulate Mn concentrations. Shell Mn/Ca ratios thus were not controlled by dissolved or particulate Mn concentrations. In *M. edulis*, the double-peak seasonal variation of shell Mn/Ca ratios was remarkably similar to the seasonal variation of shell growth rates. However, the influence of shell growth rate on shell Mn/Ca ratios is the opposite of the inverse relationship observed unequivocally between precipitation rate and Mn partition coefficient in synthetic inorganic calcite, and thus must reflect a physiological influence on shell Mn content.