Coupled clumped isotope and Mg/Ca measurements in foraminifera: Implications for palaeothermometry and seawater chemistry

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The temperature-dependent incorporation of Mg into the calcitic shells of foraminifera is a widely utilised palaeothermometer. However, the short residence time of Ca in the ocean (~1 Ma) means that seawater Mg/Ca cannot be assumed to be the same as present before the Pleistocene. The control exerted by seawater Mg/Ca on Mg incorporation during biologically-mediated carbonate precipitation is poorly understood, introducing large errors into palaeoclimate reconstructions. It has been frequently assumed that seawater-shell Mg/Ca are linearly related, yet this remains largely untested and is not the case for inorganic calcite. Moreover, the sensitivity of the Mg/Ca thermometer may also vary with seawater chemistry. If this is the case, then even relative temperature shifts over geological events may be called into question.

In order to address this, we present detailed calibrations of the relationship between seawater Mg/Ca, shell chemistry and temperature in the widely-utilised planktic foraminifera *Globigerinoides ruber* and the shallow-dwelling benthic species *Operculina ammonoides*. We show that the combined effects of seawater Mg/Ca and temperature exert a complex control on the Mg distribution coefficient, with the implications that the sensitivity of this thermometer at below-modern Mg/Ca seawater ratios is not invariant. Specifically, we find a 20% reduction in the exponential component of a Mg/Ca-temperature calibration at a seawater Mg/Ca ratio of 3.4 mol mol^{-1} (65% of modern). Both absolute Mg/Ca-derived temperatures and relative temperature changes should not be reported before the Pleistocene unless these relationships are characterised for the species of interest.

Finally, we explore the application of coupled clumped isotope and Mg/Ca measurements in shallow-dwelling large benthic foraminifera. This technique provides a method of validating Mg/Ca-derived palaeotemperatures of coeval planktic species when seawater Mg/Ca was below modern, whilst simultaneously enabling accurate reconstruction of secular seawater chemistry variation.