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0.1 The role of carbonate ion in proxies: calibrations for benthic foraminiferal Mg/Ca palaeothermometry and the carbonate ion hypothesis

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Benthic foraminiferal Mg/Ca ratios were determined on one hundred and forty one core-top samples from the Atlantic Ocean, the Norwegian Sea, the Indian Ocean, the Arabian Sea and the Pacific Ocean, mostly at sites with bottom water temperatures below 5 ^{o}C. Mg/Ca ratios are consistently lower, by $\sim$ 0.2 mmol/mol, in samples cleaned using oxidative and reductive steps than using oxidative cleaning. Within-genera differences in *Cibicidoides* species have been identified: Mg/Ca of *C. robertsonianus* $>$ *C. kullenbergi* $>$ *C. wuellerstorfi*. Comparison with bottom water temperatures for sites above $\sim 3^{o}$C support existing calibrations for *Cibicidoides and Uvigerina* species based on warm water sites as well as observations of lowered Mg/Ca at temperature below $\sim 3^{o}$C relative to that predicted by published calibrations derived over a larger temperature range. Inspection of hydrographic data shows that this temperature coincides with an order of magnitude increase in the oceanic $\Delta[CO_3^{2-}]/\Delta T$ gradient at colder temperatures An empirical sensitivity of $\Delta[CO_3^{2-}]$ on Mg/Ca has been established for *Cibicidoides wuellerstorfi* and *Uvigerina* spp. of Δ(Mg/Ca)/$\Delta[CO_3^{2-}]$ $\sim$ 0.01 mmol/mol/μmol/kg. A novel calibration using modern temperatures and Last Glacial Maximum temperatures derived via pore-fluid modelling supports a carbonate

ion saturation state effect on Mg incorporation: Mg/Ca at the LGM from the deep S. Pacific is similar to the modern calibration whereas Mg/Ca at the LGM from a site in Glacial North Atlantic Intermediate water is higher. The carbonate ion effect influences seawater δ^{18}O and temperature for cold-water sites at a ratio of about 0.2 ‰/^{o}C such that a $\sim$20 /μmol/kg lowering of $\Delta[CO_3^{2-}]$ would anomalously lower temperature by 0.5 ^{o}C and seawater δ^{18}O by about 0.1 ‰, $\sim$10m sea level equivalent.