

## Thermodynamic basis for the Mg/Ca paleotemperature proxy

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Magnesian calcite is perhaps the best studied solid solution in existence due to the widespread use of the Mg/Ca proxy to reconstruct ocean surface water paleotemperatures. Decades of experimental studies primarily based on synthetic Mg-calcite growth experiments have given us a wide range in purported equilibrium Mg distribution coefficients in calcite ( $K_d^{\text{Mg}} = ([\text{Mg}]/[\text{Ca}]_{\text{solid}})/([\text{Mg}]/[\text{Ca}]_{\text{fluid}})$ ) from ~0.01 to 0.05 at 25°C and 1 atm. These distribution coefficients are at least an order of magnitude higher than values estimated from reconstructions of pore fluid Ca and Mg profiles in marine carbonate sediments.<sup>1</sup> This dramatic disagreement makes it impossible to predict the expected temperature dependence of Mg/Ca in calcite, to understand the susceptibility of high and low magnesian calcite to diagenesis, or to critically interpret the well-established Mg/Ca paleoproxy.

The key difficulty in solving the thermodynamics of magnesian calcites is the fact that Mg partitioning behavior is highly rate dependent, and extremely slow calcite growth rates of  $<10^{-8.5} \text{ mol m}^{-2} \text{ s}^{-1}$  currently inaccessible in the laboratory are required to determine the equilibrium  $K_d^{\text{Mg}}$ .<sup>2</sup> Very slow calcite growth occurs during the recrystallization of marine sedimentary carbonates, so these materials present an ideal system to probe the thermodynamics of Mg calcite.

We present spatially resolved measurements of the Mg contents of authigenic calcite precipitated under near-equilibrium conditions from the Oceanic Drilling Program site 807 and use these data to determine the equilibrium temperature dependence of  $K_d^{\text{Mg}}$  of Mg-calcite (< 20 mol% Mg) in seawater down to 2°C. Surprisingly, we find that our thermodynamic results agree very well with the field-based foraminiferal Mg/Ca paleotemperature proxy derived by Elderfield & Ganssen,<sup>3</sup> despite the prevalence of vital effects that tend to complicate paleoproxy interpretation. We believe these findings resolve the longstanding dispute over the thermodynamics of Mg-calcite in seawater, providing a sound theoretical basis for the Mg/Ca paleotemperature proxy.

<sup>1</sup>Higgins & Schrag, 2012, *Earth Planet. Sci. Lett.* **357-358**.

<sup>2</sup>Mavromatis et al., 2013, *Geochim. Cosmochim. Acta* **114**.

<sup>3</sup>Elderfield & Ganssen, 2000, *Nature* **405**