The blocking temperature for 'clumped' isotope thermometry in aragonite

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It is challenging to reconstruct thermal histories of rocks below ~300 °C due to the common failure of minerals to reach heterogeneous equilibrium. Carbonate clumped isotope thermometry (homogeneous equilibrium of isotopologues in carbonate minerals) is potentially useful in this temperature range, but requires an understanding of the blocking temperature of this approach — the temperature below which isotopic reording is slow relative to geologic temperature changes. An important new concept we explore here is that blocking temperatures of multiple co-existing carbonate minerals might be used to constrain temperature-time history (i.e., a form of 'geospeedometry') more usefully than one could do using one mineral alone.

Previous studies show carbonate-apatite, calcite and dolomite have blocking temperatures of approximately 150°C, 200°C, and 300°C, respectively. However, aragonite has not been previously studied in detail. We conducted experiments in which aragonite crystals are heated with a known head space pressure of CO_2 for controlled temperatures and times, and changes in their clumped isotope composition were determined after quenching to room temperature. XRD analysis is being used to quantify the amount of recrystalization from aragonite to calcite, such that isotopic reordering and lattice reorganization can be related to one another.

Initial results suggest that aragonite exhibits non-first-order kinetics, simliar to previous observations for calcite [1, 2]. Measurable changes in temperature have been recorded in as little as 1 hour at 200°C, and large changes (10's of % approach to equlibrium) occur at higher temperatures over hour time scales. Rates of re-ordering slow significantly after 24 hours, perhaps suggesting the two-step diffusion/reaction mechanim suggested by Stolper [1]. Initial results suggest a closure temperature for aragnonite 10's of degrees lower than calcite (i.e., similar to or lower than carbonate-apatite). We will discuss the usefullness of these data for interpretation of previous and new measurements of clumped isotope temperatures of natural aragonites, and illustrate through models how these data could be used for geospeedometry.

[1] Stolper and Eiler, accepted, *American Journal of Science*.
[2] Passey and Henkes (2012), *EPSL*.