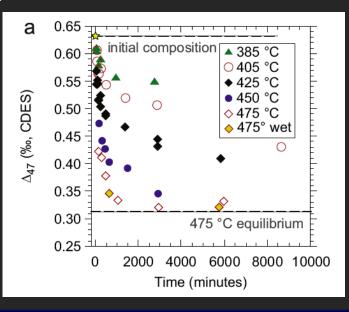
Developing a carbonate clumped isotope geothermometer

In carbonate minerals, solid-state diffusion can lead to changes in the concentration of isotopic 'clumps' (¹³C and ¹⁸O in the same carbonate molecule). The reaction forms the basis of an isotopic thermometer that increasingly leans to the right with decreasing temperature.

 $Ca^{13}C^{16}O_3 + Ca^{12}C^{18}O^{16}O_2 \leftrightarrow Ca^{13}C^{18}O^{16}O_2 + Ca^{12}C^{16}O_3$

With support from ACS–PRF, we examined the kinetics of the solid-state ¹³C-¹⁸O reordering reaction. We determined Arrhenius parameters allowing the reaction rate to be predicted as a function of temperature.



The first-order rate equation can be combined with the Arrhenius equation to predict the extent of clumped isotope reordering during heating at a specific temperature for a specific length of time.

$$\ln\left[\frac{\Delta_{47}^{t} - \Delta_{47}^{eq}}{\Delta_{47}^{init} - \Delta_{47}^{eq}}\right] = \ln\left[1 - \frac{\Delta_{47}^{init} - \Delta_{47}^{t}}{\Delta_{47}^{init} - \Delta_{47}^{eq}}\right] = \ln[1 - F] = -kt$$

$$k_T = K_o \exp\left(-E_a/RT\right)$$

The solid-state reordering process can also be used to record cooling rates of exhumed strata or rock units cooling after metamorphism. The final state of ¹³C-¹⁸O clumping of a rock gives it's apparent equilibrium temperature T_{ae} , which is a function of cooling rate.

