almost +10°C. So far, the obtained data do not form a clear trend with any measured parameter, and no clear clustering in $\Delta 47$ among different types of speleothems or caves is visible. However, the data suggest that stalactites have a similar clumped isotope composition to their corresponding stalagmites, which, if it holds true, would suggest that the clumping signal is set either when the water enters the cave or even prior to this point in the epikarst.

Experimental studies of C-O bond reordering in calcite: Relevance to preservation and thermal history of carbonates
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Solid-state reordering of C-O bonds in carbonate minerals is a process that becomes important at high temperatures. From the standpoint of paleoclimate reconstruction, this process will act to reset paleotemperatures to higher apparent temperatures during deep burial or transient heating events. For understanding the thermal histories of high temperature carbonates such as diagenetic and hydrothermal carbonates, this process will control the cooling-rate-dependent 'closure temperature', and will determine the temperature range where carbonates might record primary temperatures. By analogy with studies of C and O self-diffusion in carbonate minerals, it should be possible to conduct experiments to reveal rates of C-O reordering at several different temperatures, thereby permitting estimation of activation energies $E_a$ and preexponential coefficients $A_0$. Armed with these Arrhenius parameters, it will be possible to calculate how $\Delta 47$ compositions of carbonates evolve in response to any imaginable heating and cooling schedule.

With this goal, we have conducted ~160 heating experiments on three different calcites over temperatures ranging from 120°C to 800°C and durations of 30 minutes to ~40 days. The majority of work was done on a shallow groundwater calcite spar that was reacted under CO₂ gas under dry, low pressure conditions. We observed that this material does not follow a simple first-order, single-component reaction progress: the early reaction is faster, and the late reaction slower, than would be predicted by such a model. The reaction can be accurately modeled as a three-component system, where each component follows a first-order reaction progress. Microprobe data show that this material separates into three or more groups in Mn and Mg concentration, suggesting that the intrinsic diffusivity with respect to C-O bond reordering may be sensitive to mineral chemistry, and consistent with a three-component model of reordering behavior. However, experimental work on a different material that is compositionally homogeneous in Mn and Mg—an optical calcite from Minas Gerais, Brazil—also reveals multi-component behavior. Thus the suite of defects in a mineral, ranging from point defects to grain boundaries, might also influence C-O reordering kinetics, and progressive annealing or annihilation of such defects during heating experiments could lead to progressive elimination of mechanisms for C-O reordering, thereby giving rise to apparent multi-component behavior.

We use the Arrhenius parameters determined for the groundwater spar to model $\Delta 47$ evolution during burial and exhumation, and during cooling of initially high-temperature carbonates. These models predict that $\Delta 47$ values of climate archives will be altered at burial depths greater than ~4 km ($T > 140°C$, assuming a 25°C/km geothermal gradient and burial/exhumation rates of 0.5 km / 10Ma). Closure temperatures range from ~270°C to 140°C for cooling rates between 1°C/y and 1°C/Ma, respectively. However, we emphasize that these figures are specific to one
material, and we have demonstrated that different materials have different susceptibilities to reordering. In this context, important task will be to characterize the kinetics of a variety of materials of different chemistry and structure. Finally, preliminary experiments under wet, high-P conditions (100 MPa) suggests that C-O bond reordering rates are insensitive to pressure and presence/absence of water.

A “Direct” Method for Measuring $\Delta_{47}$ in Calcitic Fossils Indicates Cold Tropical Sea Surface Temperatures During a Large Silurian $\delta^{13}$C Excursion

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The relationship between equilibration temperature and abundance of the mass 47 doubly substituted isotopologue $^{13}$C$^{16}$O$^{18}$O in CO$_2$ gas is demonstrated using a “direct” method. While not as efficient as the automated, “heated gas line” approach (Ghosh et al., GCA 2006; Huntington et al., J. Mass Spectrometry 2009), the “direct” method relies on a comparison of gases extracted by acid digestion of carbonates to their exact stochastic counterparts obtained by heating the same gas sample to 1,000°C. In addition, our approach can be applied using a standard triple Faraday collector setup for CO$_2$, and therefore has the potential for making carbonate clumped isotope studies accessible to a larger number of institutions and investigators. Calibration of this version of the carbonate-clumped isotope paleothermometer was achieved using CO$_2$ gas produced from phosphoric acid digestion of modern biogenic carbonates formed at known temperatures. The results fall within error of the original carbonate clumped isotope paleothermometer calibration of Ghosh et al., (GCA 2006).

We used this method to test the hypothesis that large positive carbon isotope excursions of early Paleozoic age, coincident with changes in deep water and shelf lithologies, and the abundance, diversity and extinction rates of benthic and planktic organisms, are the result of atmospheric CO$_2$ drawdown and concomitant global cooling resulting from increased burial of organic matter (Jeppsson, J. Geo. Soc. 1990; Cramer & Saltzman, P$^3$ 2005). We selected atrypid brachiopod calcite from the peak of the largest such Silurian event (the Hoburgen Secundo [Arid] Episode, where the $\delta^{13}$C of oceanic DIC reached +8‰) and obtained a mean $\Delta_{47} = 0.687 \pm 0.014$ indicating a water temperature of 16 ± 3 °C. These samples are taken from a location known to have a very mild thermal history, evidenced by the lack of alteration in conodonts from the same beds. Using this temperature to calculate the isotopic composition of water in which these brachiopods grew in results in $\delta^{18}$O$_{\text{water}} < -3‰$, significantly lighter than present-day values and those derived from the composition of ophiolites (Holmden and Muehlenbachs, Science 1993).