The "clumped isotope" paleotemperature method for carbonates

Oxygen isotope geochemistry from the 1950s onward offered the potential to determine the temperature at which a mineral such as calcite precipitated from solution, if one could independently constrain the $\delta^{18}O$ value of the water from which the mineral precipitated. However, without knowledge of the $\delta^{18}O$ of the precipitating water, one was left only with an array of possible pairs of temperatures and water compositions. Reasonable assumptions about water composition could limit the range of these pairs, but there was no unique answer to the question of temperature and water composition.

That situation began to change in the early 2000s with understanding and measurement of scarce carbonate groups containing both ^{13}C and ^{18}O. Previous isotope geochemistry of carbonates had considered the isotopologue with only the light and abundant isotopes ($^{12}C^{16}O^{16}O$, with mass 44) and the two less common isotopologues with one heavy scarce isotope each ($^{13}C^{16}O^{16}O$ and $^{12}C^{18}O^{16}O$, with masses 45 and 46). The new "clumped isotope" approach focused instead on the very rare isotopologue with two scarce heavy isotopes ($^{13}C^{18}O^{16}O$ with mass 47). Measuring the abundance of this isotopologue requires a mass spectrometer that collects not only the three ions beams of conventional C-O mass spectrometry (44, 45, and 46) but also the three ion beams for masses 47, 48, and 49. The latter three additionally require much more sensitive detection because the number of ions reaching them is much smaller.

The abundance of the $^{13}C^{18}O^{16}O$ isotopologue in a given sample is expressed with the parameter Δ_{47}, which is the difference in per mil between the 47/44 ratio in the sample and the 47/44 ratio expected in a random distribution all the C and O isotopes among all the possible CO_2 isotopologues. The significance of this parameter to paleotemperature studies is that it has a one-to-one relationship with the temperatures at which $CaCO_3$ samples of both calcite and aragonite are known to have been deposited, where that relationship is

$$\Delta_{47} = 0.0592 \times 10^6 \times T^{-2} - 0.02 \qquad \text{(T in Kelvins)}$$

and gives the graphic relationship shown below. The result is the Holy Grail of stable isotope paleothermometry: a unique paleotemperature from a $CaCO_3$ sample. It also allows calculation of the $\delta^{18}O$ of the precipitating water, yielding a double reward in paleoclimate studies where both temperature and nature of the precipitating water are of interest.

Eiler, J.M., and Schauble, E., 2004. $^{18}O^{13}C^{16}O$ in Earth's atmosphere: *Geochimica et Cosmochimica Acta,* v. 68, p. 4767-4777.

Ghosh, P., et al., 2006, ^{13}C-^{18}O bonds in carbonate minerals: a new kind of paleothermometer: *Geochimica et Cosmochimica Acta,* v. 70, p. 1439-1456.

Came, R.E., et al., 2007, Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic era: *Nature,* v. 449, p. 198-201.

Affek, H.P., et al., 2008, Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry: *Geochimica et Cosmochimica Acta,* v. 72, p. 5351-5360.