Paleoclimate reconstruction from speleothem fluid inclusions - are isotope ratios really preserved?

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Isotope ratios ($\delta^{18}O$, $\delta^{17}O$, δD) of water-containing fluid inclusions are increasingly used as proxy for past mineral formation conditions. Fluid inclusion isotope ratios are particularly promising for speleothems as they can provide unique and direct insight into past climatic conditions at the Earth's surface. A fundamental question arises with regard to the preservation of the oxygen isotope ratio in fluid inclusions. Temperature changes affect the equilibrium isotope fractionation. Accordingly, the isotope ratios in fluid inclusions may change over time following temperature variations even after enclosure of the inclusion in the mineral matrix.

Two different laboratory experiments were conducted to assess the question of isotopic re-equilibration in fluid inclusions. One experiment was prepared with a high water/calcite ratio, a super saturation close to zero (no net dissolution or precipitation) and a strong isotopic gradient between calcite and water. This experiment suggested the related time scales of the isotopic re-equilibration between fluid and mineral surface not to be below the order of months. In a second experiment the isotope ratios of a fluid inclusion analogue were investigated following the effect of a strong temperature change (17 K). This gives an upper limit for isotopic changes related to variations in the mean annual temperature over glacial/interglacial cycles or after speleothem removal from cave sites.