



Oxygen isotope fractionation processes in the water-calcite-aragonite system

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The O isotopic composition of speleothems in their pure calcite or pure aragonite polymorphs provides valuable insight into past climate variability. However, robust climatic interpretations become difficult when both polymorphs are present either in different growth layers or as intergrown fabrics. Experimental studies show that the O isotope fractionation between the dissolved carbonate species and CaCO_3 is about 0.75‰ (at 10°C) larger for aragonite than for calcite (e.g., Kim et al., 2007, Kim and O'Neil, 1997). The temperature dependence of this offset is negligible for temperature variations typical of most cave systems. However, cave analogue experiments examining this offset are still lacking.

Here, we present stable O isotope measurements of a Holocene speleothem from the Swiss Alps, which shows exactly one calcite-aragonite transition along individual growth layers. Oxygen isotope measurements along 'Hendy test'-like traverses across those transitions provide insight into the fractionation behavior of the water-calcite vs. water-aragonite system. We observed a fractionation offset smaller than predicted by laboratory experiments that varies by at least a factor of two. In addition, the observed variations correlate positively with growth rate and negatively with the isotopic composition of the calcite precipitating at the growth axis.

The reason for this behavior is still unclear. Trace element analyses across the transitions of growth layers are planned to help understanding this pattern.