

Investigating kinetic effects on clumped isotopes during formation of (speleothem) calcite: insights from cave analogue laboratory experiments

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We present results from cave-analogue laboratory experiments investigating the temporal evolution of clumped isotope values (Δ_{47}) during precipitation of (speleothem) calcite for the dissolved inorganic carbon (DIC) as well as the precipitated CaCO_3 . During the experiments, thin solution films of a supersaturated $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ solution with a thickness of ca. 0.1 mm are caused to flow down an inclined sand-blasted glass or marble plate, progressively precipitating CaCO_3 along the flow path. After different distances of flow and, thus, residence times on the plates, pH, electrical conductivity and the Δ_{47} values of the DIC as well as the directly precipitated CaCO_3 are determined using the same samples and methods as in Hansen et al. (2019)^[1]. This enables us to study the temporal evolution of the Δ_{47} values of both the DIC and the CaCO_3 as a function of the experimental conditions, such as temperature, pCO_2 and precipitation rate^[2]. The Δ_{47} values at the beginning of the plates (i.e., at 0 cm distance of flow, comparable to the apex of a stalagmite) reflect the experimental temperatures according to Kluge et al. (2015)^[3]. With increasing distance of flow and thus progressive precipitation, we observe strong disequilibrium effects in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and Δ_{47} . The corresponding Δ_{47} values deviate towards higher apparent temperatures. We aim to quantify kinetic effects on the Δ_{47} values for speleothem calcite and – eventually – to develop together with $\delta^{18}\text{O}$ a correction technique. This is essential in terms of quantitative reconstruction of past climate variability in natural samples.

^[1]Hansen et al. 2019, Chem. Geol. 509: 20-44.

^[2]Hansen et al. 2017. GCA 211, 28-47.

^[3]Kluge et al., 2015, GCA 157, 213-227.