SIMULATING FORMATION OF SPELEOTHEM CALCITE IN THE LABORATORY: INVESTIGATING KINETIC STABLE ISOTOPE FRACTIONATION

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We present the results of laboratory experiments aiming to quantify the processes affecting the $\delta^{13}C$ and $\delta^{18}O$ values in speleothems during precipitation of calcite, similar to those occurring on the surface of a speleothem. During the experiments, a thin film (≈ 0.1 mm) of a $CaCO_3$-CO_2-H_2O solution, supersaturated with respect to calcite, flows down an inclined marble or sand-blasted glass plate, progressively precipitating $CaCO_3$ along the flow path. After different residence times on the plates, the drip water is sampled and pH, electrical conductivity as well as the $\delta^{13}C$ and $\delta^{18}O$ values of the dissolved inorganic carbon (DIC) and the precipitated $CaCO_3$ are determined. This enables to investigate the fractionation between *all* different species involved in precipitation process ($CaCO_3$, HCO_3^-, CO_2 and H_2O) as a function of, e.g., temperature or precipitation rate under cave analogue conditions[1]. We observe a negative fractionation between HCO_3^- and $CaCO_3$ and a dependence on precipitation rate for both $\delta^{13}C$ and $\delta^{18}O$, documenting kinetic isotope fractionation. The oxygen isotope fractionation between drip water and precipitated $CaCO_3$ and its dependence on the temperature is in agreement with observations from calcite farmed in situ in caves.[2]

[1] Hansen, M., Scholz, D., Froeschmann, M.-L., Schöne, B. R., and Spötl, C., 2017. Carbon isotope exchange between cave air and thin solution films on speleothem surfaces: Artificial cave experiments and a complete diffusion-reaction model. Geochimica et Cosmochimica Acta 211, 28-47

[2]Tremaine, D.M., P.N. Froelich, and Y. Wang, Speleothem calcite farmed in situ: Modern calibration of $\delta^{18}O$ and $\delta^{13}C$ paleoclimate proxies in a continuously-monitored natural cave system. Geochimica et Cosmochimica Acta, 2011. 75: p. 4929-4950.