

## Simulating speleothem growth in the laboratory: Determination of stable isotope fractionation factors during precipitation of speleothem calcite

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We present laboratory experiments aiming to understand the processes affecting the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of speleothems during precipitation of calcite from a thin layer of solution. In particular, we determined the precipitation rates and the isotope fractionation factors in dependence of several parameters, such as temperature, cave  $\text{pCO}_2$  and supersaturation with respect to calcite. The experiments were performed in a climate box in order to simulate cave conditions and to control them during the experiments<sup>[1]</sup>.

In the experiments, a thin film of a  $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ -solution supersaturated with respect to calcite flew down an inclined marble surface or a sand-blasted borosilicate glass plate, and the drip water was sampled at different distances and, thus, residence times on the plate. Subsequently, pH, electrical conductivity and the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the dissolved inorganic carbon (DIC) as well as the precipitated  $\text{CaCO}_3$  were determined. In addition, we determined the stable isotope values of the drip water and the atmosphere inside the box during the experiments. This enabled the identification of carbon and oxygen isotope fractionation factors between all carbonate species. The experiments were conducted at 10, 20 and 30 °C, a  $\text{pCO}_2$  of 1000 and 3000 ppmV and with a  $\text{Ca}^{2+}$  concentration of 2 and 5 mmol/l.

We observed an exponential decay of conductivity with increasing distance of flow documenting progressive precipitation of calcite confirming previous observations<sup>[2]</sup>. The corresponding time constants of precipitation range from 180 to 660 s. Both the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values show a progressive increase along the flow path. The enrichment of the  $\delta^{13}\text{C}$  values seems to be strongly influenced by kinetic isotope fractionation, whereas the  $\delta^{18}\text{O}$  values are in the range of isotopic equilibrium. The fractionation between the precipitated  $\text{CaCO}_3$  and DIC is between -1 and -6.5 ‰ for carbon isotopes ( $^{13}\epsilon$ ) and between -1.5 and -3 ‰ for oxygen isotopes ( $^{18}\epsilon$ ). The temperature-dependent oxygen isotope fractionation between the precipitated  $\text{CaCO}_3$  and the water was in good agreement with previously reported values<sup>[3]</sup>.

[1] Dreybrodt, W., M. Hansen, and D. Scholz, Processes affecting the stable isotope composition of calcite during precipitation on the surface of stalagmites: Laboratory experiments investigating the isotope exchange between DIC in the solution layer on top of a speleothem and the  $\text{CO}_2$  of the cave atmosphere. *Geochimica et Cosmochimica Acta*, 2016. 174: p. 247-262.

[2] Hansen, M., W. Dreybrodt, and D. Scholz, Chemical evolution of dissolved inorganic carbon species flowing in thin water films and its implications for (rapid) degassing of  $\text{CO}_2$  during speleothem growth. *Geochimica et Cosmochimica Acta*, 2013. 107: p. 242-251.

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