

# **Simulating speleothem growth in the laboratory: Determination of stable isotope fractionation factors and their dependence on temperature and precipitation rate**

D. SCHOLZ<sup>1\*</sup>, M. HANSEN<sup>1</sup>, B.R. SCHÖNE<sup>1</sup> AND  
C. SPÖTL<sup>2</sup>

<sup>1</sup>Institute of Geosciences, University of Mainz,  
Germany (\*correspondence: scholzd@uni-  
mainz.de, m.hansen@uni-mainz.de,  
schoeneb@uni-mainz.de)

<sup>2</sup>Institute of Geology, University of Innsbruck,  
Austria (christoph.spoetl@uibk.ac.at)

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 thin films of solution. The experiments are conducted in a climate box enabling us to control temperature, humidity,  $\text{pCO}_2$  and the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of atmospheric  $\text{CO}_2$  [1].

In the experiments, a thin (ca. 0.1 mm) film of a solution supersaturated with respect to calcite flows down an inclined marble or sand-blasted glass plate, progressively precipitating calcite along the flow path. The drip water is sampled at different distances of flow and, thus, residence times on the plates, and pH, electrical conductivity as well as the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the dissolved inorganic carbon (DIC) and the precipitated  $\text{CaCO}_3$  are determined. This enables us for the first time to determine the carbon and oxygen isotope fractionation factors between *all* involved carbonate species ( $\text{CaCO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_2$ ) and water and their dependence on the experimental parameters. The experiments were conducted at 10, 20 and 30 °C, a  $\text{pCO}_2$  of 1000 and 3000 ppmV and with  $\text{Ca}^{2+}$  concentrations of 2 and 5 mmol/l, respectively.

Both the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values show a progressive increase along the flow path, which can be quantitatively described by a model based on Rayleigh distillation of the  $\text{HCO}_3^-$  reservoir [2]. The carbon and oxygen isotope fractionation between  $\text{HCO}_3^-$  and  $\text{CaCO}_3$  shows a strong dependence on precipitation rate documenting kinetic isotope fractionation. The oxygen isotope fractionation between the precipitated  $\text{CaCO}_3$  and water is in good agreement with the values determined from calcite formed in situ in caves [3].

[1] Dreybrodt et al. (2016) *Geochim Cosmochim Ac* 174, 247-262. [2] Scholz et al. (2009) *Geochim Cosmochim Ac* 73, 2592-2602. [3] Tremaine et al. (2011) *Geochim Cosmochim Ac* 75, 4929-4950.