Determination of (kinetic) stable carbon and oxygen isotope fractionation factors for speleothem calcite

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The most widely applied climate proxies in speleothems are stable carbon and oxygen isotopes ($\delta^{13}C$ and $\delta^{18}O$) which can be measured at high temporal resolution. The interpretation of these signals in terms of past climate variability, however, is complex because various processes occurring in the soil, the epikarst and inside the cave may affect both $\delta^{13}C$ and $\delta^{18}O$ values [1].

Here we present laboratory experiments aiming to understand the basic physical and chemical processes affecting the $\delta^{13}C$ and $\delta^{18}O$ values during precipitation of $CaCO_3$ on the surface of a stalagmite. We (i) test whether calcite precipitation occurs under conditions of isotopic equilibrium and (ii) determine the fractionation factors in dependence of the experimental parameters, such as temperature, supersaturation with respect to calcite and cave pCO_2.

In our experiments, thin films of a $CaCO_3$-CO_2-H_2O-solution supersaturated with respect to calcite flow down an inclined $CaCO_3$-plate or sandblasted borosilicate glass plate. Dripwater is sampled at different flow distances and, thus, different residence times on the plate. Afterwards, pH, electrical conductivity and the $\delta^{13}C$ and $\delta^{18}O$ values of the DIC are determined. We observe an exponential decay of conductivity documenting progressive precipitation of calcite [2]. The corresponding precipitation time is ca. 500 s. Both, the $\delta^{13}C$ and $\delta^{18}O$ signals show an increase along the flow path due to progressive precipitation of $CaCO_3$ and degassing of CO_2. We also determine the $\delta^{13}C$ and $\delta^{18}O$ values of the precipitated calcite. This enables the determination of fractionation factors between the DIC and the precipitated $CaCO_3$. First results show strong kinetic fractionation for carbon isotopes, whereas the fractionation of oxygen isotopes are in the range of the equilibrium values.

[1] Dreybrodt and Scholz (2011), *Geochim. Cosmochim. Acta* **75**, 734-752. [2] Hansen et al. (2013), *Geochim. Cosmochim. Acta* **105**, 242-251.