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Kinetic fractionation of stable isotopes in speleothems – results from modelling and laboratory experiments

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The stable isotope composition of speleothems is influenced by climate related parameters and, thus, widely applied for paleoclimate reconstructions. However, several studies have shown that effects resulting from kinetic isotope fractionation may also have a significant influence (Hendy, 1971; Mickler et al., 2006).

Here, the δ^{13}C enrichment between cave drip water and speleothem calcite is described by a box model simulating isotopic fractionation under equilibrium as well as disequilibrium conditions (Mühlinghaus et al., submitted). The isotopic enrichment is modelled both along individual growth layers and the stalagmite growth axis, and the modelled values are in the range observed in natural speleothems. Our results show that speleothem δ^{13}C is influenced by drip rate, temperature and mixing between the solution film on top of the stalagmite and the impinging drop, with drip rate and mixing having a comparable influence, which is larger than the influence of temperature.

In principle, the kinetic enrichment of δ^{18}O can be modelled analogically to δ^{13}C. However, there are two problems: (i) The oxygen isotopic composition of HCO_3^- is buffered by the oxygen reservoir within H_2O (i.e. hydration and hydroxylation reactions), and (ii) the oxygen isotopic fractionation factors for DIC species are not precisely known. Thus, modelling of speleothem δ^{18}O is associated with substantial uncertainty at present.

To determine the effects of kinetic isotope fractionation on speleothem δ^{18}O, several laboratory experiments were performed (Wiedner et al., submitted). In these experiments, synthetic calcite is precipitated under controlled conditions (i.e. temperature, drip rate, isotopic composition of the drip water and humidity). Two kinds of experiments were conducted: (i) Calcite precipitation in beakers simulating slow degassing of CO_2 (i.e. fractionation under equilibrium conditions) and (ii) precipitation along an inclined glass channel simulating fast degassing of CO_2 (i.e. fractionation under disequilibrium conditions). The results show that the kinetic enrichment of both $\delta^{13}C$ and $\delta^{18}O$ is related to the drip rate. The laboratory experiments should allow to quantify the effects of isotope buffering and potentially enable the modelling of the enrichment of speleothem $\delta^{18}O$.

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