

Modelling the temporal evolution of the $\delta^{13}\text{C}$ values during precipitation of speleothem calcite by a complete diffusion-reaction model

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It has been known since the late 1960's that speleothem calcite - in most cases - does not precipitate in stable isotope equilibrium with the drip water and the dissolved inorganic carbon. Thus, the conventionally used equilibrium carbon and oxygen isotope fractionation factors cannot be used to calculate stable isotope fractionation within the thin films of solution on the surface of a speleothem.

Two models have been developed to describe the temporal evolution of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values within the thin film [1, 2]. Although both models are based on very different basic assumptions, they provide relatively similar results for the majority of calcite precipitated between two subsequent drops [3]. However, both models utilise equilibrium stable isotope fractionation factors and have not been experimentally validated yet.

Here we present a novel complete diffusion-reaction model, considering the temporal evolution of all species of DIC (CO_2 , HCO_3^- , CO_3^{2-}), precipitation and dissolution of speleothem calcite at the water-mineral interface, potential changes in pH, rapid degassing of CO_2 as well as carbon isotope exchange with cave CO_2 . This model enables us to describe the temporal evolution of speleothem $\delta^{13}\text{C}$ values without the assumptions of the aforementioned models. We show the dependence on temperature, precipitation rate and cave pCO_2 and compare the output with the existing models [4].

[1] Dreybrodt (2008), *Geochimica et Cosmochimica Acta* 72, 4712-4724. [2] Scholz, Mühlinghaus & Mangini (2009), *Geochimica et Cosmochimica Acta* 73, 2592-2602. [3] Dreybrodt & Scholz (2011), *Geochimica et Cosmochimica Acta* 75, 734-752. [4] Dreybrodt & Romanov (2016), *Geochimica et Cosmochimica Acta* 195, 323-338.