



# Simulating speleothem growth in the laboratory: Determination of the stable isotope fractionation ( $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ) between $\text{H}_2\text{O}$ , DIC and $\text{CaCO}_3$

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## ARTICLE INFO

Editor: E. B Michael

### Keywords:

Speleothem  
Stable carbon isotopes  
Stable oxygen isotopes  
Stable isotope fractionation  
Laboratory experiments  
Synthetic calcite

## ABSTRACT

Here we present novel cave-analogue experiments directly investigating stable carbon and oxygen isotope fractionation between the major involved species of the carbonate system ( $\text{HCO}_3^-$ ,  $\text{CO}_2$ ,  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$ ). In these experiments, which were performed under controlled conditions inside a climate box, a thin film of solution flew down an inclined marble or glass plate. After different distances of flow and, thus, residence times on the plate, pH, electrical conductivity, supersaturation with respect to calcite, precipitation rate as well as the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of the dissolved inorganic carbon (DIC) and the precipitated  $\text{CaCO}_3$  were obtained.

Progressive precipitation of  $\text{CaCO}_3$  along the plate is accompanied by degassing of  $\text{CO}_2$  and stable isotope fractionation, and the system is driven out of isotope equilibrium. We observe a strong enrichment of the  $\delta^{13}\text{C}$  values with increasing residence time and a smaller enrichment in  $\delta^{18}\text{O}$ . The temporal evolution of the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of both the DIC and the precipitated  $\text{CaCO}_3$  can be explained by a Rayleigh fractionation model, but the observed enrichment in  $\delta^{13}\text{C}$  values is much larger than expected based on isotope equilibrium fractionation factors.

Our setup enables to determine the fractionation between  $\text{CaCO}_3$  and  $\text{HCO}_3^-$ , i.e.,  $\epsilon_{\text{CaCO}_3/\text{HCO}_3^-}$ . Carbon isotope fractionation,  $^{13}\epsilon_{\text{CaCO}_3/\text{HCO}_3^-}$ , is strongly negative for all experiments and much lower than equilibrium isotope fractionation (0–1‰). In addition,  $^{13}\epsilon_{\text{CaCO}_3/\text{HCO}_3^-}$  decreases with increasing residence time on the plate, and thus decreasing supersaturation with respect to calcite. Thus, isotope fractionation depends on precipitation rate and consequently occurs under kinetic conditions. This is in contrast to previous studies, which found no rate-dependence and no or even a positive carbon isotope fractionation between  $\text{CaCO}_3$  and  $\text{HCO}_3^-$ . Oxygen isotope fractionation,  $^{18}\epsilon_{\text{CaCO}_3/\text{HCO}_3^-}$ , is also negative and dependent on precipitation rate. Since no literature values for  $^{18}\epsilon_{\text{CaCO}_3/\text{HCO}_3^-}$  are available, we calculated  $^{18}\epsilon_{\text{CaCO}_3/\text{HCO}_3^-}$  using equilibrium oxygen isotope fractionation factors between water and calcite and water and  $\text{HCO}_3^-$ , respectively. At the beginning of the plate, the fractionation is in agreement with the fractionation calculated using fractionation factors determined in cave systems.

The observed fractionation between  $\text{CaCO}_3$  and water,  $1000\ln^{18}\alpha$ , is also in good agreement with the values determined in cave systems and shows a very similar temperature dependence  $1000\ln^{18}\alpha = 16.516(\pm 1.267) * \frac{10^3}{T} - 26.141(\pm 4.356)$ . However, with progressive precipitation of  $\text{CaCO}_3$  along the plate, the system is forced out of isotope equilibrium with the water, and  $1000\ln^{18}\alpha$  increases.

The large, negative, rate-dependent isotope fractionations observed in this study suggest that precipitation of speleothem calcite is strongly kinetically controlled and may, thus, have a large effect on speleothem  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. Since these values may erroneously be interpreted as reflecting changes in past temperature, precipitation and/or vegetation density, these results have important implications for paleoclimate reconstructions from speleothems.

## 1. Introduction

Speleothems are unique paleoclimate archives providing important

information on past climate variability in a wide range of climatic zones (Fairchild and Baker, 2012). They can be dated very precisely using U-series disequilibrium methods (Richards and Dorale, 2003; Scholz and

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<https://doi.org/10.1016/j.chemgeo.2018.12.012>

Received 31 October 2017; Received in revised form 13 December 2018; Accepted 17 December 2018

Available online 21 December 2018

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