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ISOLUTION 1.0: an ISotope evoLUTION model describing the stable oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) isotope values of speleothems

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Abstract: Stable oxygen and carbon isotope ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) are the most applied climate and environmental proxies in speleothems allowing to infer past changes in cave drip water $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ related to climate and environmental variations from above the cave. However, disequilibrium isotope fractionation processes can modify $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in speleothems, which is in most cases difficult to estimate due to inter-dependencies on various cave specific parameter. To better understand the effect of these disequilibrium isotope fractionation processes proxy system models were developed in recent years, such as the ISOLUTION model. Here the code of the ISOLUTION model is made available for the public and the speleothem community to be applied to research questions that arise from e.g. monitoring programs that investigate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of in situ calcite precipitates on watch glasses or modern speleothem calcite, respectively. Another application of the ISOLUTION model is to investigate the dependence of calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ on the variation of one or multiple cave specific parameter, such as cave air temperature, drip interval, cave air pCO_2 , Ca^{2+} concentration of the drip water as well as on relative humidity and wind velocity. This allows to quantitatively estimate the effect of disequilibrium isotope fractionation processes in individual caves and drip sites on speleothem $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for modern and past climates and may help to further elucidate the complex interplay of kinetic and disequilibrium isotope fractionation.

Keywords: speleothems, proxy system model, ISOLUTION

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INTRODUCTION

Speleothems are valuable continental archives of past climate and environmental change (Fairchild & Baker, 2012). Their greatest advantages are that they can be dated with very high precision by U-series disequilibrium methods (Richards & Dorale, 2003; Cheng et al., 2013) and that they preserve a variety of climate and environmental proxies, such as stable oxygen and carbon isotopes and trace elements (McDermott, 2004; Fairchild & Treble, 2009; Lachniet, 2009). The interpretation of these proxy time series is not always straightforward since the proxy signals in speleothems depend on a complex interplay of processes occurring in or between the atmosphere, the soil and karst above the cave as well as inside the cave (McDermott, 2004; Fairchild & Treble, 2009; Lachniet, 2009; Dreybrodt & Scholz, 2011). However, in most cases the variation of speleothem proxy time

series can be linked to past climate changes when the signal-to-noise ratio is very high, i.e., the climate related signal in speleothems overprints any other variations, such as variations in oxygen isotope ratios to changes in the Asian Monsoon (Cheng et al., 2016) or the South American Monsoon (Cruz et al., 2005). Another example are the analyses of stable oxygen isotopes in Central European winter precipitation ($\delta^{18}\text{O}_p$), which depend on the North Atlantic Oscillation (Baldini et al., 2008b; Deininger et al., 2016) – the dominating mode of atmospheric climate variability in Europe in winter (Hurrell, 1995). Deininger et al. (2016) show that changes in $\delta^{18}\text{O}_p$ dominate speleothem $\delta^{18}\text{O}$ signals in Central Europe and that speleothems from Central Europe can be utilised to reconstruct the NAO.

In the last decades, various models have been developed quantitatively describing the processes of CaCO_3 dissolution and precipitation (both above

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and inside the cave, Hendy, 1971; Buhmann & Dreybrodt, 1985a, b; Dreybrodt, 1988), the processes that determine the growth rate and the shape of speleothems (Baker et al., 1998; Dreybrodt, 1999; Kaufmann, 2003; Kaufmann & Dreybrodt, 2004; Mühlinghaus et al., 2007; Romanov et al., 2008a) as well as the processes that determine the preserved stable isotope signals in speleothems (Mühlinghaus et al., 2007; Dreybrodt, 2008; Romanov et al., 2008b, Mühlinghaus et al., 2009; Scholz et al., 2009; Wackerbarth et al., 2010; Dreybrodt & Scholz, 2011; Fohlmeister et al., 2011a, b; Deininger et al., 2012; Dreybrodt & Deininger, 2014). The development of proxy system models that account for in-cave isotope fractionation processes was in large part performed by the speleothem research group DAPHNE (www.fg-daphne.de). The aim of DAPHNE was to improve the quantitative understanding of speleothem proxy signals with a focus on stable oxygen and carbon isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) and their dependence on climate and environmental variations from above the cave as well as on cave specific parameters, such as cave air temperature, drip rate and soil and cave air pCO_2 . DAPHNE conducted, amongst other activities, extensive cave monitoring programs (Riechelmann et al., 2011), performed experiments with synthetic carbonates (Wiedner et al., 2008; Polag et al., 2010) and developed proxy system models for carbon (^{13}C and ^{14}C) and oxygen (^{18}O) isotope signals in cave drip water (Wackerbarth et al., 2010; Fohlmeister et al., 2011a). A particular focus of DAPHNE was to gain a better understanding of the stable carbon and oxygen isotope fractionation processes during the formation of speleothems, i.e., during the precipitation of calcite, when the stable carbon and oxygen isotope signal of the cave drip water is preserved in the speleothem. In this context, a proxy system model was developed to describe the temporal evolution of the oxygen and carbon isotope ratios in a carbonic solution on the surface of a speleothem during calcite precipitation, the ISOTOpe evoLUTION model (ISOLUTION).

ISOLUTION is coded in MATLAB® and performs a variety of complex, iterative calculations (see below for details). So far, the results of the model have been made available to the community by corresponding publications (Mühlinghaus et al., 2007, 2009; Scholz et al., 2009; Deininger et al., 2012). These enable the reader to derive and understand the qualitative relationships resulting from the model (e.g., that a reduced drip rate – or an increased drip interval – results in increasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of speleothem calcite). However, quantitative information on specific questions are difficult to obtain from these publications alone. In addition, due to the complex interplay of the different processes, the response to a synchronous change in several parameters (e.g., soil pCO_2 , cave pCO_2 and drip rate), which is usually the case in natural cave systems, is impossible to derive from the examples discussed in the literature.

Here we make the MATLAB® code of the ISOLUTION model available for the public and the speleothem community – but also to other scientific communities, such as climate modellers and researchers working

on data-model comparison. In the following sections, we briefly discuss the basic equations of the model (geochemistry and isotope geochemistry) and the relationships between the individual parameters and the modelled stable oxygen and carbon isotope ratios.

DESCRIPTION OF THE ISOLUTION MODEL

The ISOLUTION model calculates the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the calcite precipitated at the tip of a stalagmite (i.e., at the growth axis of the stalagmite) from a carbonic solution (i.e., containing dissolved inorganic carbon, DIC) that is super-saturated with respect to calcite. This carbonic solution is fed by water that drips from the cave ceiling and is referred to as cave drip water in the following. ISOLUTION accounts for isotope fractionation processes during the precipitation of calcite that we refer to as disequilibrium isotope fractionation or effects in the following. We emphasise that disequilibrium isotope fractionation should not be confused with kinetic isotope fractionation. Kinetic isotope fractionation is – in comparison to equilibrium isotope fractionation – described by a different (kinetic) isotope fractionation factor, α_k . Kinetic isotope fractionation effects include for example the relationship of α_k for ^{18}O with the calcite precipitation rate and pH that is observed in beaker experiments by (Dietzel et al., 2009). In case of the dependence of α_k on the calcite precipitation rate alternative theoretical models are proposed inferring that the ratio of the calcite precipitation rate and the dissolution rate (DePaolo, 2011; Watkins et al., 2014) or the molecular diffusion of oxygen isotopes (Watson, 2004) in the calcite crystal are responsible for the observed relationships. In contrast, disequilibrium isotope fractionation accounts for all (chemical and isotope) reactions/processes between molecules participating in the reaction of calcite precipitation, which disturb the isotope equilibrium between the individual molecules. These include the conversion of HCO_3^- to CO_2 , H_2O and CaCO_3 (calcite) during calcite precipitation (Eq. 1) (Mühlinghaus et al., 2009; Scholz et al., 2009), the oxygen isotope exchange between H_2O and HCO_3^- during the hydration and hydroxylation of CO_2 (Scholz et al., 2009) or the oxygen isotope fractionation during the evaporation and condensation of H_2O from the solution layer or the cave air, respectively (Deininger et al., 2012; Dreybrodt & Deininger, 2014). Thus, disequilibrium isotope effects can result in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values deviating from the value expected for isotope equilibrium. Theoretical and empirical studies infer that the degree to which disequilibrium isotope effects alter the equilibrium $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in speleothems in dependence on cave specific parameters varies with the drip interval (Mühlinghaus et al., 2009; Deininger et al., 2012; Riechelmann et al., 2013). Therefore, these effects are expected to be important for drip sites where the drip interval is long and/or varies between short and long values (see below for a detailed discussion).

This section is subdivided into two paragraphs: First, we briefly introduce the basics of the geochemistry of the $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ -system (2.1.1) and the isotope

mass balance model (2.1.2). Then (2.2) we explain the individual functions of the ISOLUTION model. A list of

parameters used by the ISOLUTION model and in the following text is given in Table 1.

Table 1. Nomenclature of parameters used by the ISOLUTION model.

Nomenclature		
	Variable	Explanation
Model variables	$\delta^{13}\text{C}$	Carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$) of the drip water DIC (HCO_3^-) expressed in the delta-notation relative to VPDB [per mil]
	$\delta^{18}\text{O}$	Oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$) of the drip water (H_2O) expressed in the delta-notation relative to VSMOW [per mil]
	T_c	Cave air temperature [$^{\circ}\text{C}$]
	d	Drip interval [s], i.e., the time between two subsequent drops dripping from the cave ceiling
	$p\text{CO}_{2,\text{cave}}$	$p\text{CO}_{2,\text{cave}}$ [ppmV]: CO_2 partial pressure of the cave air
	$p\text{CO}_{2,\text{drip}}$	$p\text{CO}_{2,\text{drip}}$ [ppmV]: the equivalent of the $p\text{CO}_2$ required to get the Ca^{2+} concentration of the cave drip water. This $p\text{CO}_2$ level can be calculated from the Ca^{2+} concentration [mol/l] prior to the application of ISOLUTION using the MATLAB function CALPCO2.m. Note that no other ions, such as Sr^{2+} and Mg^{2+} are taken into account.
Other parameters used in the manuscript or by the ISOLUTION model	Φ	The mixing parameter describes the mixing between the new, impacting drip and the existing solution on the surface of the speleothem. Due to splashing effects, the contribution of the new drop to the solution may be variable. A mixing parameter of 1 means that the new drop contributes 100% to the existing solution, i.e., it replaces the entire old solution. $\Phi = 0.5$ means that the new solution contains 50% of the previous solution and 50% of the new drop (see Mühlinghaus et al., 2007; 2009, for details).
	T_K	Cave air temperature [K]
	α_y	α_y is the isotope fractionation factor between two species. x indicates the respective isotope system, i.e., 18 for oxygen isotopes and 13 for carbon isotopes. y describes the corresponding physical or chemical reaction. For instance, if y is calcite/ H_2O , the fractionation factor refers to isotope fractionation between water and calcite.
	R_y	R denotes the isotope ratio. As for fractionation factors, x is 18 for the oxygen isotope system and 13 for the carbon isotope. y describes the corresponding physical or chemical reaction, e.g., $^{18}\text{R}_{\text{HCO}_3^-}$ is the oxygen isotope ratio of bicarbonate (HCO_3^-).
	$\delta^x Z_y$	$\delta^x Z_y$ is the expression of the isotope ratios in the delta notation ($\delta^x Z_y = xR_y / xR_{\text{st}} - 1$). $^{18}\text{R}_{\text{st}}$ is the value for internationally accepted standards (VPDB for all carbon bearing species and VSMOW for water). Note that $\delta^x Z_y$ is $\delta^{18}\text{O}_y$ for oxygen isotopes and $\delta^{13}\text{C}_y$ for carbon isotopes.
	N_y	N [mol] is the molar mass of species y
	n_y	n [mol/l] is the concentration of species y
	T	time [s]
	τ_p	τ_p is the characteristic time constant for the precipitation of calcite. $\tau_p = \delta / \lambda_p$ is calculated from the thickness, δ , of the solution layer on the speleothem surface and the rate constant λ_p . λ_p depends on temperature. This value are taken from Dreybrodt and Scholz (2011), based on calculations (Baker et al., 1998).
	τ_{OEX}	τ_{OEX} is the characteristic time constant for oxygen isotope exchange between water and HCO_3^- and is taken from Dreybrodt and Scholz (2011), based on experiments by Beck et al. (2005).

Theoretical background

Geochemistry

The ISOLUTION model is based on the chemical equations of the $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ -system (e.g., Dreybrodt 1988) including the chemical equilibrium between Ca^{2+} and HCO_3^- with CaCO_3 , CO_2 , and H_2O (Eq. 1). This equation basically describes the precipitation (and dissolution) of CaCO_3 in case of a chemical disequilibrium between the right and left-hand side of the equation:



Note that Eq. (1) is valid for the majority of cave systems, where the cave drip water has a pH-value of ca. 8 and the DIC mainly consists of HCO_3^- .

For calcite precipitation (i.e., stalagmite growth), the temporal evolution of the Ca^{2+} concentration of the cave drip water at the tip of the stalagmite is given by (Eq. 2) (Kaufmann, 2003):

$$\text{Ca}^{2+}(t) = (\text{Ca}^{2+}(t_0) - \text{Ca}_{\text{ap}}^{2+}) \cdot e^{-t/\tau_p} + \text{Ca}_{\text{ap}}^{2+} \quad (2)$$

whereat Ca^{2+} is the calcium concentration, $\text{Ca}_{\text{ap}}^{2+}$ is the apparent Ca^{2+} concentration (both in mol/l), τ_p is the time constant for calcite precipitation and t is the time (both in seconds). The temporal evolution of the Ca^{2+} concentration depends on the initial Ca^{2+} concentration of the cave drip water, $\text{Ca}^{2+}(t_0)$, which is defined as the Ca^{2+} concentration at time $t_0 = 0$ s, when the drip impinges on the speleothem surface. The initial Ca^{2+} concentration is determined mainly by the available CO_2 during the CaCO_3 dissolution in the karst (Hendy, 1971), which is parameterised by the drip water CO_2 in ISOLUTION (i.e., the required CO_2 partial pressure in air to obtain an observed Ca^{2+} concentration in the cave drip water). The apparent Ca^{2+} concentration, $\text{Ca}_{\text{ap}}^{2+}$, denominates the 'equilibrium' Ca^{2+} concentration of the drip water with respect to the cave $p\text{CO}_2$ and inhibiting effects during calcite precipitation. It is calculated by

$\text{Ca}^{2+}_{\text{ap}} = \text{Ca}^{2+}_{\text{eq}}/\sqrt{0.8}$, whereat $\text{Ca}^{2+}_{\text{eq}}$ is the Ca^{2+} concentration with respect to the cave air pCO_2 and the factor $1/\sqrt{0.8}$ accounts for the inhibiting effects (Dreybrodt et al., 1997; Kaufmann, 2003). Therefore, the amount of excess Ca^{2+} ($\text{Ca}^{2+}(t_0) - \text{Ca}^{2+}_{\text{ap}}$) that is available for calcite precipitation and speleothem formation, respectively, depends on the difference between the drip water pCO_2 and cave air pCO_2 . The precipitation rate constant, λ_p , is approximated by a cubic spline (Eq. 3) using the values of Dreybrodt & Scholz (2011), which are based on the results of Baker et al. (1998) who used the theoretical model for calcite precipitation derived by Buhmann & Dreybrodt (1985a, b) and Dreybrodt (1988, 1999):

$$\lambda_p = (1.188 \cdot T_C^3 - 1.29 \cdot T_C^2 + 787.5 \cdot T_C + 4844) \cdot 10^{-11} \left[\frac{\text{m}}{\text{s}} \right] \quad (3)$$

T_C is the cave air temperature in °C. Typical values for τ_p are c. 2,000, 740, and 350 s for cave air temperature of 0, 10, and 20°C, respectively. These values are found to be in good agreement with empirical observations (Baker et al., 1998) and have been used also in other studies that investigate growth rate related effects in speleothem stable isotope time series (Baldini et al., 2008a).

A similar equation can be derived for the evolution of the HCO_3^- concentration by considering the condition of electro neutrality (Eq. 4):

$$\text{HCO}_3^-(t) = (\text{HCO}_3^-(t_0) - \text{HCO}_{3\text{ap}}^-) \cdot e^{-\tau_p t} + \text{HCO}_{3\text{ap}}^- \quad (4)$$

HCO_3^- is the HCO_3^- concentration of the solution (mol/l) and $\text{HCO}_{3\text{ap}}^-$ is the apparent HCO_3^- concentration (both in mol/l). The time constant of calcite precipitation (τ_p) is determined by Δ/λ_p : Δ is the thickness of the solution film at the tip of the stalagmite, and λ_p is the precipitation rate constant for a film thickness of 100 μm (Eq. 3). Both τ_p and time (t) are measured in seconds.

Carbon and oxygen isotope geochemistry

The calculation of speleothem calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values by the ISOLUTION model is based on a multi-box mass-balance approach, first described by Rayleigh (1902), which has been used to calculate the change of isotope ratios in various disciplines of isotope geochemistry (Mook & de Vries, 2000; Mook, 2006). The fundamental principle of this mass-balance approach is that the number (amount) of rare isotopes (e.g., ^{18}O or ^{13}C) is constant for the entire system at all times (i.e., a closed system) irrespective of the individual isotope fractionation (or its 'strength') processes and the geochemical reactions within the system. For calcite precipitation (Eq. 1), this means that even if the total number of ^{18}O atoms contained in the HCO_3^- reservoir changes with time during precipitation of calcite, the total number of ^{18}O atoms contained in the whole system (i.e., HCO_3^- , CO_2 , H_2O , and CaCO_3) is constant. We note that the Rayleigh approach forming the basis of ISOLUTION has been a matter of debate for several years (Dreybrodt & Scholz, 2011; Dreybrodt, 2016; Dreybrodt & Romanov, 2016). However, the intention of this paper is to outline the basic principles of ISOLUTION and to make it available

to the public rather than a critical discussion of its basics. In this context, the reader is referred to the corresponding publications (Dreybrodt & Scholz, 2011; Dreybrodt, 2016; Dreybrodt & Romanov, 2016).

In general, an isotope ratio, R , is defined as the ratio between the rare and the abundant isotope of the same element, which are in the case of stable oxygen and carbon isotopes, $^{18}\text{R} = ^{18}\text{O}/^{16}\text{O}$ for oxygen and $^{13}\text{R} = ^{13}\text{C}/^{12}\text{C}$ for carbon isotopes. These ratios are usually translated into the δ -notation by reporting the relative deviation of the isotope ratio from a standard (R_{st}): $\delta = (R/R_{\text{st}} - 1)$. In case of the ISOLUTION model, the VPDB standards are used for carbonates, and the VSMOW standard for water.

Here we recall the very basic mass balance multi-box model, which only accounts for one process/reaction progressively removing molecules from a reservoir (e.g., evaporation of water from a pond; Eq. 5). This process is accompanied by isotope fractionation described by the isotope fractionation factor α . Furthermore, the educt is assumed to be removed instantaneously to permit any further interaction with the reservoir. Note that it is not removed from the system because this would be a violation of the mass balance. Considering a reservoir of N molecules (e.g., H_2O or HCO_3^-) with an isotope ratio R_0 at time $t_0 = 0$ s, from which molecules are progressively removed at a specific rate dN (note that the rate can change with time as it is the case for calcite precipitation, Eq. 2) by a certain process or reaction (e.g., evaporation of water), the equation for the mass balance of the rare isotopes is given by:

$$\frac{R \cdot N}{1 + R} = \frac{(R + dR)}{1 + R + dR} - \frac{\alpha \cdot R \cdot dN}{1 + \alpha \cdot R} \quad (5)$$

The term on the left-hand side of the equation is the number of rare isotopes before the mass or number of molecules, dN , has been removed from the reservoir, whereas the right-hand side is the sum of the number of rare isotopes remaining in the reservoir and the number of rare isotopes that were removed. To a good approximation, $(1 + R + dR)$ and $(1 + \alpha R)$ are $\approx (1 + R)$ because dR is much smaller than R and α is approximately 1. Further, if products of differentials are neglected, Eq. (5) can be simplified to Eq. 6a and 6b, respectively.

$$R \cdot N \approx R \cdot N + N \cdot dR + R \cdot dN + \alpha \cdot R \cdot (-dN) \quad (6a)$$

$$0 \approx N \cdot dR + R \cdot dN + \alpha \cdot R \cdot (-dN) \quad (6b)$$

The solution of this differential equation (Eq. 6b), which describes the temporal evolution of the isotope ratio, R , of the reservoir is then given by:

$$R(t) = R_0 \cdot \left(\frac{N(t)}{N_0} \right)^{\alpha-1} \quad (7)$$

Equation 7 describes the temporal evolution of the isotope ratio R of the reservoir, which depends on the isotope ratio and the number of molecules at time $t = 0$ s, R_0 , and N_0 , the temporal evolution of the number of molecules, $N(t)$, whereat t is the time, and the isotope fractionation factor α . If the mass balance is more complicated than this example, which is the case for the CO_2 - H_2O - CaCO_3 -system, it is also possible from Eq. (6b) to calculate the change of the isotope

ratio of the reservoir, dR , and the new isotope ratio of the reservoir, R_{new} , as follows:

$$dR = (\alpha - 1)R_{\text{old}} \cdot \frac{dN}{N} \Rightarrow R_{\text{new}} = R_{\text{old}} + dR \quad (8)$$

In Eq. 8, dR is the change in the isotope ratio of the molecules in the reservoir that is caused by the removal of molecules described by dN , which is accompanied by isotope fraction effects. The change of the isotope ratio dR depends on the isotope ratio before the removal of molecules, R_{old} , as well as on the relative change of the molecules (dN/N) and the isotope fractionation factor α . A similar approach can be inferred for the weighted mean isotope ratio of the fraction removed from the reservoir (e.g., the precipitated calcite) by summing up all fractions weighted by the number of molecules dN removed from the reservoir. This is necessary because the reaction/mass rates can change with time like it is the

case for calcite precipitation, where dN progressively decreases with time (Eq. 2).

The previous example is the most simple mass balance model. However, it nicely shows the mathematical structure of the ISOLUTION model. ISOLUTION accounts for additional processes/reactions and has more reservoirs (Table 2). In detail, the current version of ISOLUTION includes reservoirs for HCO_3^- , liquid and vaporous H_2O (H_2O_l and H_2O_v). The processes and reactions included in the ISOLUTION model are the precipitation of calcite (P1), the oxygen isotope exchange between H_2O_l and HCO_3^- (P2) and the evaporation of liquid water (H_2O_l) as well as the condensation of water vapour (H_2O_v) (P3). We refer to the original publications for a detailed derivation of the individual mass balance models for each reservoir and the discussion of the results (Mühlinghaus et al., 2007, 2009; Scholz et al., 2009; Deininger et al., 2012).

Table 2. Summary of reservoirs (R) and physical and chemical processes (P) potentially affecting the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ value of calcite accounted for in the ISOLUTION model.

Number	Reservoirs and reactions/processes	Relevance	Explanation	Publication
¹⁸ R1 ¹³ R1	HCO_3^-	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	HCO_3^- reservoir	(Mühlinghaus et al., 2007) (only $\delta^{13}\text{C}$) (Mühlinghaus et al., 2009)
¹⁸ R2	H_2O_l	$\delta^{18}\text{O}$	Reservoir of liquid water	(Mühlinghaus et al., 2009) (Scholz et al., 2009) (Deininger et al., 2012)
¹⁸ R3	H_2O_v	$\delta^{18}\text{O}$	Reservoir of water vapour	(Deininger et al., 2012)
¹⁸ P1.1 ¹³ P1.1	$\text{HCO}_3^- \rightarrow \text{CaCO}_3$	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	Conversion of HCO_3^- into calcite during precipitation of calcite	(Mühlinghaus et al., 2007) (only $\delta^{13}\text{C}$) (Mühlinghaus et al., 2009) (Scholz et al., 2009)
¹⁸ P1.2 ¹³ P1.2	$\text{HCO}_3^- \rightarrow \text{CO}_2$	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	Conversion of HCO_3^- into dissolved CO_2 during precipitation of calcite	(Mühlinghaus et al., 2007) (only $\delta^{13}\text{C}$) (Mühlinghaus et al., 2009) (Scholz et al., 2009)
¹⁸ P1.3	$\text{HCO}_3^- \rightarrow \text{H}_2\text{O}_l$	$\delta^{18}\text{O}$	Conversion of HCO_3^- into liquid H_2O during precipitation of calcite	(Mühlinghaus et al., 2009) (Scholz et al., 2009)
¹⁸ P2.1	$\text{HCO}_3^- \rightarrow \text{H}_2\text{O}_l$	$\delta^{18}\text{O}$	Oxygen isotope exchange between HCO_3^- and liquid H_2O	(Mühlinghaus et al., 2009) (Scholz et al., 2009)
¹⁸ P2.2	$\text{H}_2\text{O}_l \rightarrow \text{HCO}_3^-$	$\delta^{18}\text{O}$	Oxygen isotope exchange between HCO_3^- and liquid H_2O	(Mühlinghaus et al., 2009) (Scholz et al., 2009)
¹⁸ P3.1	$\text{H}_2\text{O}_v \rightarrow \text{H}_2\text{O}_l$	$\delta^{18}\text{O}$	Condensation of vaporous H_2O	(Deininger et al., 2012)
¹⁸ P3.1	$\text{H}_2\text{O}_l \rightarrow \text{H}_2\text{O}_v$	$\delta^{18}\text{O}$	Evaporation of liquid H_2O	(Deininger et al., 2012)

The average isotope ratio of the calcite precipitated during a specific time interval (e.g., between two subsequent drops) is calculated as the weighted mean of the isotope ratio of the precipitated calcite that has been converted from HCO_3^- (Eq. 9):

$$\bar{R} = \frac{\sum_i dN(t_i) \cdot R_{\text{calcite}}(t_i)}{\sum_i dN(t_i)} \quad (9)$$

The calcite isotope ratio at time t_i , $R_{\text{calcite}}(t_i)$ (Eq. 10), is calculated from the isotope ratio of HCO_3^- , $R_{\text{HCO}_3^-}$, and the isotope fractionation factor for the conversion of HCO_3^- to calcite ($\alpha_{\text{calcite}/\text{HCO}_3^-}$).

$$\begin{aligned} R_{\text{calcite}}(t_i) &= \alpha_{\text{calcite}/\text{HCO}_3^-} \cdot R_{\text{HCO}_3^-}(t_i) = \\ &= \alpha_{\text{calcite}/\text{H}_2\text{O}} \cdot \alpha_{\text{H}_2\text{O}/\text{HCO}_3^-} \cdot R_{\text{HCO}_3^-}(t_i) \end{aligned} \quad (10)$$

The isotope fractionation factor, $\alpha_{\text{calcite}/\text{HCO}_3^-}$, is derived from the combination of the isotope fractionation factors for $\text{HCO}_3^- \rightarrow \text{H}_2\text{O}$ ($\alpha_{\text{H}_2\text{O}/\text{HCO}_3^-}$) and $\text{H}_2\text{O} \rightarrow \text{calcite}$ ($\alpha_{\text{calcite}/\text{H}_2\text{O}}$). See section 2.2 for a more detailed discussion.

MATLAB-functions of the ISOLUTION model

The ISOLUTION model consists of nine individual functions (Table 3) programmed in MATLAB®. These are subdivided into different levels: level 0 functions start a routine, whereas higher level functions are invoked by lower level functions. In the following, the individual functions are briefly described.

CALPCO2.m

Function CALPCO2.m converts Ca^{2+} concentrations (given in mol/l) in a pCO_2 -equivalent using the mass laws of the CO_2 - H_2O - CaCO_3 -system assuming a chemical equilibrium between all chemical species. CALPCO2.m does not consider any other ions occurring in natural cave drip waters, such as Mg^{2+} . CALPCO2.m firstly calculates the Ca^{2+} concentrations for pCO_2 values ranging from 0 to 1,000,000 ppmV subdivided into ten equidistant intervals (i.e., the Ca^{2+} concentration for 0, 100,000, 200,000 ppmV, etc.). In a second step, the function finds the interval mirroring

Table 3. ISOLUTION MATLAB® functions.

#	Function	Level
1	CALPCO2.m	0
2	ISOLUTION.m	0
3	ISOTOPE_CALCITE.m	1
4	ISOTOPE_EVOLUTION.m	2
5	ISOTOPE_EVOLUTION_MEAN.m	2
6	CONCENTRATIONS.m	2, 3
7	CONSTANTS.m	2, 3
8	EVAPORATION.m	2, 3
9	FRACTIONATION_FACTORS.m	2, 3

the real Ca^{2+} concentration (e.g., the interval from 0 to 100,000 ppmV). Then step one and two are repeated until the real and the calculated Ca^{2+} concentration are similar, i.e., the pCO_2 interval mirroring the real Ca^{2+} concentration is again subdivided into ten equidistant intervals, and then step 2 is repeated.

ISOLUTION.m

ISOLUTION.m starts the ISOLUTION model and allows the user to choose between two different options: **1)** Calculation of a single calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value for a given set of input parameters (i.e., temperature, drip interval, drip water pCO_2 (calculated by CALPCO2.m), cave air pCO_2 , relative humidity, wind velocity, mixing parameter, initial drip water $\delta^{13}\text{C}$ (of the DIC) and $\delta^{18}\text{O}$ (of liquid H_2O) values prior to calcite precipitation). The user can enter these parameters into the MATLAB command window. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are calculated by the function ISOTOPE_CALCITE.m using the values of the input parameters. **2)** Calculation of the evolution (sensitivity) of calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in dependence on a user-defined interval for one of the following input parameters: temperature, drip interval, drip water pCO_2 , cave air pCO_2 , relative humidity and wind velocity. The other input parameters are kept constant. The user again enters these values into the MATLAB command window. The calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are again calculated by the function ISOTOPE_CALCITE.m.

2.2.3 ISOTOPE_CALCITE.m

ISOTOPE_CALCITE.m calculates a single calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value for a given set of input parameters. First, the equilibrium $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the HCO_3^- at the tip of the stalagmite – which vary in dependence on the mixing parameter and other parameters – are calculated by the function ISOTOPE_EVOLUTION.m. These equilibrium values are usually established after a few drops, depending, however, on the mixing parameter (Mühlinghaus et al., 2009; Deininger et al., 2012). As a rule of thumb, the number of drops until isotope equilibrium has been established increases with decreasing mixing parameter, but is usually lower than 20. Based on these equilibrium isotope values, the temporal evolution of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the HCO_3^- is then calculated for the user-defined drip interval by the function ISOTOPE_EVOLUTION_MEAN.m. This temporal evolution is used in turn to calculate the mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the precipitated calcite.

ISOTOPE_EVOLUTION.m

ISOTOPE_EVOLUTION.m calculates the equilibrium $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of HCO_3^- , the concentration of HCO_3^- and the amount of liquid H_2O , which change in case of calcite precipitation and evaporation of water, respectively. The stable isotope and chemical equilibrium is usually established within 10 to 20 drops, respectively.

ISOTOPE_EVOLUTION_MEAN.m

ISOTOPE_EVOLUTION_MEAN.m calculates the weighted mean (Eq. 9) of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of HCO_3^- that is used to calculate the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the precipitated calcite using the isotopic and chemical equilibrium values estimated by ISOTOPE_EVOLUTION.m.

CONCENTRATIONS.m

Function CONCENTRATIONS.m calculates the equilibrium concentrations of the $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ -system in dependence of a pCO_2 value and temperature based on equations of Dreybrodt (1988).

CONSTANTS.m

CONSTANTS.m lists all constants that are used, such as the stable oxygen and carbon isotope ratios of VPDB and VSMOW, respectively.

EVAPORATION.m

EVAPORATION.m calculates the evaporation rate in dependence of temperature, relative humidity and wind velocity (Deininger et al., 2012).

FRACTIONATION_FACTORS.m

FRACTIONATION_FACTORS.m lists all stable carbon and oxygen isotope fractionation factors used by ISOLUTION (See (Deininger et al., 2012) for detail). The original publication of ISOLUTION (Deininger et al., 2012) used the fractionation factor of (Kim & O'Neil, 1997) to describe equilibrium isotope fractionation between water and calcite, $\alpha_{\text{calcite}/\text{H}_2\text{O}}$. The updated version of ISOLUTION.m described here allows the user in addition to choose between the $\alpha_{\text{calcite}/\text{H}_2\text{O}}$ values of Johnston et al. (2013), Tremaine et al. (2011), and Coplen (2007). Although different fractionation factors result in different absolute temperatures, we note that the temperature sensitivity of all fractionation factors is very similar. Hence, if ISOLUTION is applied to estimate palaeo-temperatures, the calculated relative temperature changes should be very similar irrespective of the choice of $\alpha_{\text{calcite}/\text{H}_2\text{O}}$.

RESULTS

Disequilibrium isotope fractionation effects

As outlined in the previous sections, ISOLUTION only uses equilibrium isotope fractionation factors. Thus, kinetic isotope effects, which most likely have a significant effect in many speleothems (Mickler et al., 2006; McDermott et al., 2011) are not accounted for. However, since progressive precipitation of CaCO_3 from the thin solution layer disturbs the initial carbon and oxygen isotope equilibrium (Scholz et al., 2009),

the modelled $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the precipitated speleothem calcite are not in equilibrium with the drip water initially impinging on the speleothem surface (or the water collected in the framework of cave monitoring studies). In order to avoid the common mistake in the speleothem literature that this disequilibrium is related to kinetic isotope fractionation, we use the term disequilibrium isotope fractionation throughout this paper.

The degree of isotope disequilibrium introduced to the modelled speleothem $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values strongly depends on the input parameters of the ISOLUTION model. The dependence of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the precipitated calcite on the individual cave and drip site specific parameters can be deduced from sensitivity

studies (Mühlinghaus et al., 2009; Deininger et al., 2012). Table 4 summarises the qualitative response of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values on changes of the individual parameters. For most variables, the qualitative effect is similar for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. For instance, if the drip interval increases, this results in increasing $\delta^{13}\text{C}$ as well as $\delta^{18}\text{O}$ values (Table 4). If the cave air pCO_2 increases (implying reduced supersaturation of the cave drip water with respect to calcite, Eq. 2), the resulting values will be lower for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Table 4). The exception is temperature, which has opposing effect on the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Table 4). If cave air temperature increases, speleothem calcite $\delta^{18}\text{O}$ values will be lower, whereas calcite $\delta^{13}\text{C}$ values will increase.

Table 4. Compilation of the qualitative response of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the precipitated calcite on changes of the individual cave parameters. Arrows pointing upwards (downwards) indicate increasing (decreasing) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, respectively.

Change in corresponding parameter	Temperature for $\delta^{18}\text{O}$	Temperature for $\delta^{13}\text{C}$	Drip interval	Drip pCO_2	Cave air pCO_2	Rel. humidity	Wind velocity	F
↑	↓	↑	↑	↑	↓	↓	↑	↓
↓	↑	↓	↓	↓	↑	↑	↓	↑

Beside these qualitative responses, the ISOLUTION model can be used to evaluate the importance of individual cave-specific parameters for calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values at individual cave and drip sites, respectively. For example, cave air pCO_2 will not be important if it is constant (e.g., in case of little or no cave ventilation (Riechelmann et al., 2011)). In contrast, if cave air pCO_2 varies on the order of 1000 ppmV throughout the year (Spötl et al., 2005; Matthey et al., 2008), it may have a significant effect on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of speleothem calcite. To demonstrate the application of the ISOLUTION model for such questions, we investigate the dependence of speleothem $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for a cave with the following conditions: the cave air temperature is 10°C , we consider two drip sites with very different drip intervals of 100 (drip site 1) and 1500 s (drip site 2), drip water pCO_2 is 5,000 ppmV and cave air pCO_2 is 1,000 ppmV. Furthermore, relative humidity is 100%, and we assume no wind flow (wind velocity is 0 m/s). We also assume that no mixing between the solution film on the speleothem surface and the impinging drop occurs, which corresponds to a mixing parameter, ϕ , of 1.

To investigate the effect of changes in these parameters on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the precipitated speleothem calcite, we vary them in reasonable intervals. For this simulation, we select option 2 of the ISOLUTION model and select the variable that is examined. The results are illustrated in Figure 1 (examples 1 and 2), Figure 2 (examples 3 and 4) and Figure 3 (example 5).

Example (1) Varying temperature: Cave air temperature can experience temporal variations ranging from diurnal, seasonal, annual or even longer time scales (Spötl et al., 2005; Tremaine et al., 2011). In addition, it may depend on the location inside the cave where it is recorded. We would expect that temperature vary considerably close to a cave

entrance, while temperature changes in remote chambers of a cave should be small. This has, for instance, been observed in a monitoring study of Obir Cave, a dynamically ventilated cave, where the seasonal temperature change of a chamber closest to the entrance (12 meters) is about 4°C , whereas remote chambers only experience seasonal temperature changes that are less than 0.5°C (Spötl et al., 2005). ISOLUTION modelled changes in calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ infer changes in $\delta^{18}\text{O}$ of approximately $-0.2\text{‰}/^\circ\text{C}$, whilst the corresponding change in $\delta^{13}\text{C}$ is $0.05\text{‰}/^\circ\text{C}$ (Fig. 1a and b). Hence, the observed temperature changes in Obir Cave would cause changes in $\delta^{18}\text{O}$ of about 0.8‰ in the entrance part and $<0.1\text{‰}$ in remote chambers. Changes in $\delta^{13}\text{C}$ are 0.2‰ and $<0.025\text{‰}$. We note again that the change in $\delta^{18}\text{O}$ is more or less invariant on the used fractionation factor $\alpha_{\text{calcite}/\text{H}_2\text{O}}$, because the temperature dependence is nearly identical for all fractionation factors. Furthermore, while speleothem $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values linearly respond to temperature changes for low drip intervals, the response is non-linear for long drip intervals (Fig. 1, the non-linearity cannot be resolved for $\delta^{18}\text{O}$). The reason for this non-linearity is the temperature dependence of the precipitation rate and other isotope fractionation effects during precipitation of calcite (Table 2) (Mühlinghaus et al., 2009; Deininger et al., 2012).

Example (2) Varying drip interval: Drip intervals can show by far the largest variability within caves (e.g., Genty et al., 2014), which is a result of the complexity of karst hydrology (e.g., Bradley et al., 2010) and the water balance of the atmosphere-soil-karst system, which may depend on rain- and snowfall, respectively, and evapo-transpiration – depending in turn on temperature, density and type of vegetation and soil thickness and permeability. The effect of the drip interval of different drip sites inside a single cave (short vs. long) has been shown

to directly affect the recorded speleothem $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Riechelmann et al., 2013). The reason for the dependence of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values on drip interval is related to the temporal evolution of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the dissolved HCO_3^- during the precipitation of calcite. While calcite is progressively precipitated from the drip water, isotope fractionation effects (Table 2) result in increasing $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in HCO_3^- in turn causing increased calcite $\delta^{18}\text{O}$

and $\delta^{13}\text{C}$ values (Scholz et al., 2009). With increasing drip intervals, the influence of these processes becomes stronger and result in higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Mühlinghaus et al., 2009; Deininger et al., 2012) (Figs. 1c and d). For very long drip intervals, the drip water may reach chemical equilibrium within the cave pCO_2 , and the calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values converge to an upper value that depend also on the other cave parameters (Mühlinghaus et al., 2009).

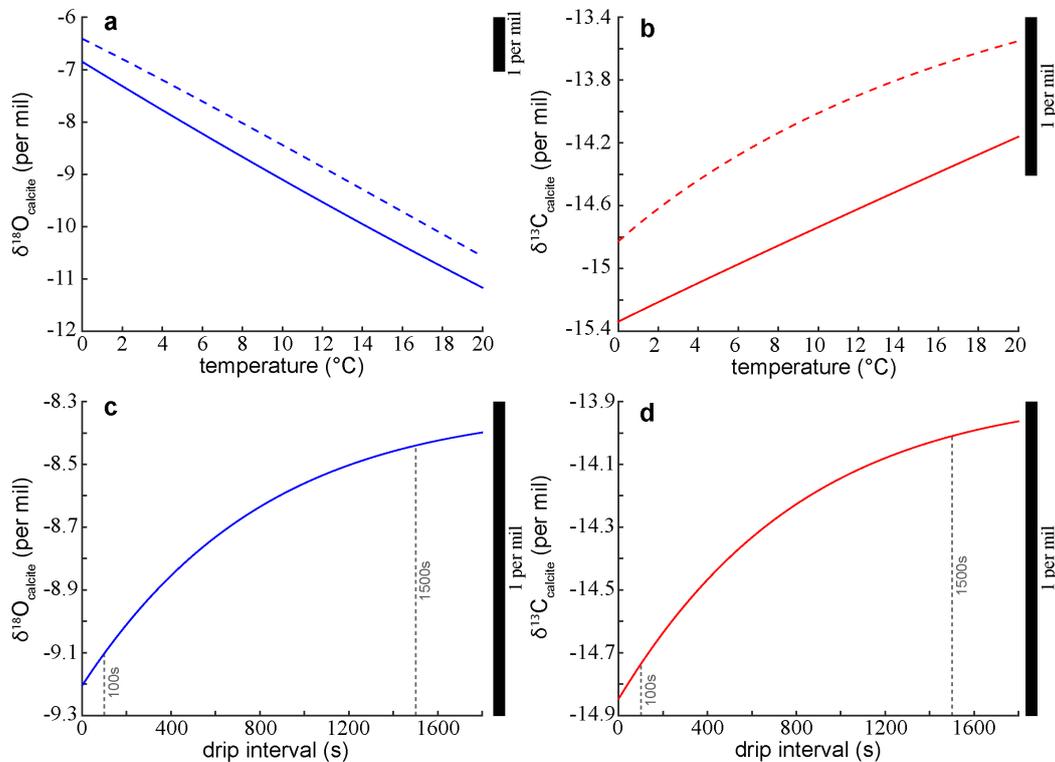


Fig. 1. Response of speleothem calcite $\delta^{18}\text{O}$ (blue) and $\delta^{13}\text{C}$ (red) values on changes in temperature and drip interval. For these experiments cave temperature is varied from 0 to 20°C (a and b) and the drip interval from 1 to 1,800 s (c and d). The drip water and cave air pCO_2 are kept constant at 5,000 and 1,000 ppmV, respectively. Furthermore, relative humidity is 100%, and we assume no wind flow (wind velocity is 0 m/s). Panels a) and b) illustrate the evolution of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in response to temperature changes for a drip interval of 100 (straight line) and 1,500 s (dashed line). Panels c) and d) show the evolution of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for varying drip interval. The black bar indicates a change of 1%.

Examples (3) and (4) Varying Ca^{2+} concentration (drip water pCO_2) and cave air pCO_2 :

The excess Ca^{2+} concentration, which is equivalent to the difference of the Ca^{2+} concentrations for the drip water pCO_2 and the cave air pCO_2 (Eq. 2) determines the maximum amount of Ca^{2+} available for calcite precipitation and in turn speleothem formation. Hence, if the drip water pCO_2 increases while the cave air pCO_2 is constant the excess Ca^{2+} concentration increases whereas if the cave air pCO_2 increases at a constant drip water pCO_2 the excess Ca^{2+} concentration decreases; and vice versa for a decreased drip water pCO_2 and a decreased cave air pCO_2 . Depending on the drip interval, the variations of the excess Ca^{2+} concentration can change the degree to which disequilibrium isotope effects modify calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. In principle, if the drip interval is longer than approximately 4 times τ_p , the entire Ca^{2+} excess is precipitated resulting in the highest calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values ($\tau_p = \delta / \lambda_p$ where δ is the film thickness and λ_p the precipitation rate, see section 2 for detail). Therefore, for a higher Ca^{2+} excesses and longer drip intervals, higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are observed (Fig. 2). Hence, for a constant

drip interval, an increasing Ca^{2+} concentration of the drip water or a higher drip water pCO_2 , respectively, results in increasing calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. In contrast, an increasing cave air pCO_2 provokes decreasing calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and vice versa. Importantly, the effect of changes in the Ca^{2+} excess becomes stronger for longer drip intervals (Fig. 2).

Example (5) Mixing effects: The carbonic solution film at the tip of the stalagmite is constantly renewed by new drops falling from the cave ceiling keeping the carbonic solution super-saturated with respect to calcite, i.e., maintaining active speleothem formation. However, it is possible that the falling drop does not replace the entire carbonic solution at the tip of the stalagmite but only a fraction, which provokes mixing of the previous carbonic solution and the new drop. This affects, on the one hand, the equilibrium concentrations of the CO_2 - H_2O - CaCO_3 -system and, on the other hand, the mean carbon and oxygen isotope ratios of the dissolved bicarbonate (Mühlinghaus et al., 2009). For instance, if the impinging drop completely replaces the carbonic solution at the tip of the stalagmite ($\phi = 1$), the initial Ca^{2+} (HCO_3^-)

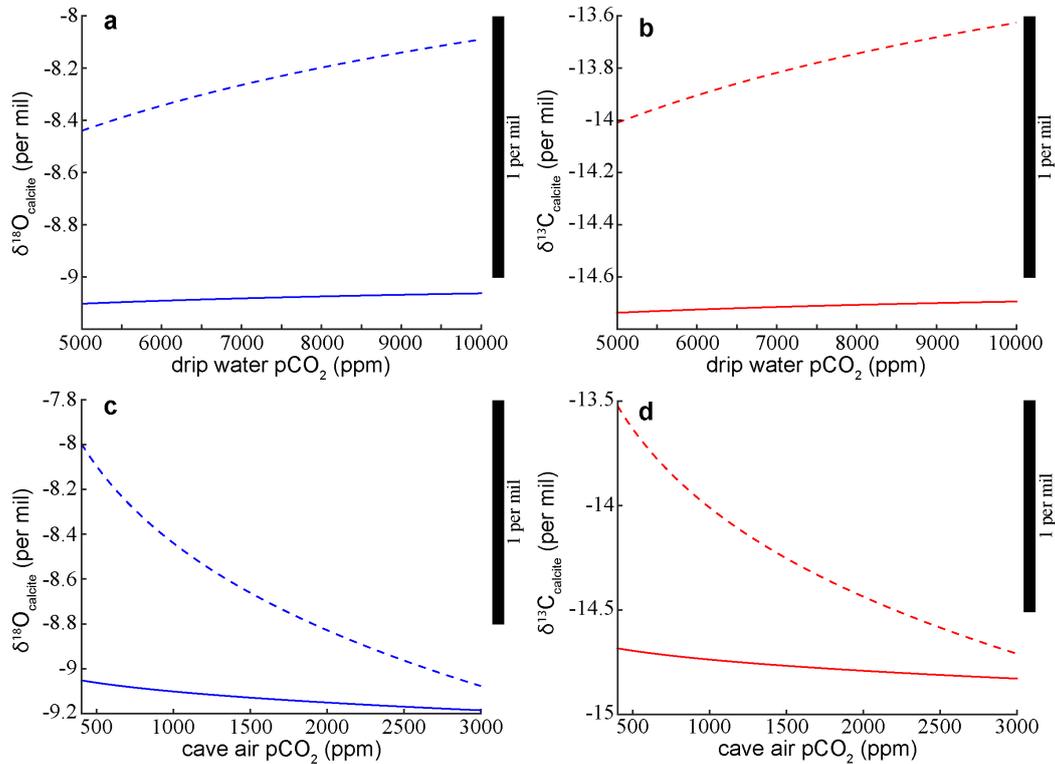


Fig. 2. Response of $\delta^{18}\text{O}$ (blue) and $\delta^{13}\text{C}$ (red) values of the precipitated calcite to changes in drip water (a and b) and cave air pCO_2 (c and d). For these experiments the drip water and cave air pCO_2 value are varied from 5,000 to 10,000 ppmV and 400 to 3,000 ppmV, respectively. The cave air temperature and the drip intervals are kept constant at 10°C and 100 s (straight line) and 1,500 s (dashed line), respectively. Furthermore, relative humidity is 100%, and we assume no wind flow (wind velocity is 0 m/s). The black bar indicates a change of 1%.

concentration and the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the carbonic solution correspond to the respective values of the drip. If, however, due to splashing effects, only a specific fraction of the impinging drop contributes to the existing solution film at the tip of the speleothem (e.g., 50%, $\phi = 0.5$), the new initial Ca^{2+} (HCO_3^-) concentration and the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are determined by a mixture of the values of the drop and the existing carbonic solution. This results in stronger disequilibrium isotope fractionation effects because of the contribution of

the existing carbonic solution, which has already been affected by progressive precipitation of calcite (Fig. 3). Note that for a very small contribution of the drip to the existing carbonic solution (e.g., $\phi = 0.1$, heavy splashing), oxygen isotope exchange between H_2O and HCO_3^- and the resulting re-establishment of oxygen isotope equilibrium between H_2O and HCO_3^- causes an attenuation of the observed disequilibrium effects. This is particularly pronounced for large drip intervals (Fig. 3a) (Mühlinghaus et al., 2009; Deininger et al., 2012).

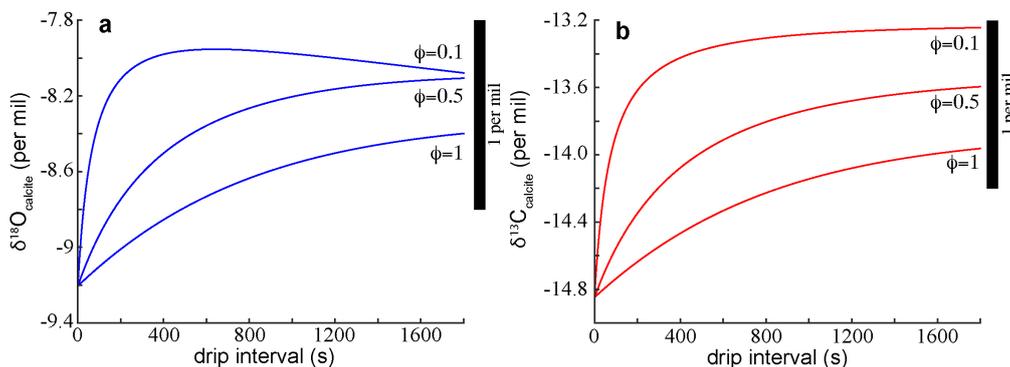


Fig. 3. Dependence of the $\delta^{18}\text{O}$ (a) and $\delta^{13}\text{C}$ (b) values of the precipitated calcite on the mixing parameter, ϕ . The black bar indicates a change of 1%.

SUMMARY AND OUTLOOK

ISOLUTION is the most complex model describing stable oxygen and carbon isotope fractionation processes during the formation of speleothems currently available. Here we make the code available to the public, which enables other researchers to estimate the effect of various cave specific parameters,

such as temperature, drip interval, cave pCO_2 or Ca^{2+} content of the drip water, on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values expected for speleothem calcite. We hope that this will result in more quantitative estimates of the effects of disequilibrium isotope fractionation in speleothem palaeoclimate studies, which are frequently mentioned to explain deviations as well as a larger variability in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values expected under conditions

of isotope equilibrium. Furthermore, we expect that the application of ISOLUTION to monitoring data (e.g., comparison of drip water data with the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of recent calcite collected in situ inside the caves) will provide further information on the current potential and limitations of ISOLUTION. One shortcoming of the current version of ISOLUTION is that it does not account for uncertainties of the cave specific parameters that result either from measurements or regressions or simply because certain parameter couldn't be measured and were estimated only. However, these uncertainties can be visualised by repeating the sensitivity analyses with varied input parameters (e.g., the minimum and maximum of the range of a cave specific parameter, e.g., temperature).

ISOLUTION does not account for real, rate-dependent kinetic isotope fractionation effects (Dietzel et al., 2009; Watkins et al., 2014). If precise and accurate kinetic isotope fractionation factors as well as their dependence on the different cave parameters become available, ISOLUTION could be extended by accounting for these processes as well. Furthermore, ISOLUTION currently neither accounts for carbon and oxygen isotope exchange between the dissolved HCO_3^- and gaseous CO_2 (Dreybrodt & Romanov, 2016; Hansen et al., 2017) nor for isotope exchange with the calcite surface. For specific cave parameters (e.g., long drip intervals, high cave pCO_2 and low concentrations of HCO_3^-), these processes may have a significant effect on the temporal evolution of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of both the dissolved HCO_3^- and the precipitated calcite. These processes may also be included in future versions of ISOLUTION. Another extension of ISOLUTION in the future can be the generation of artificial speleothem $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ time series that includes also the growth rate model of Mühlinghaus et al. (2007). This would facilitate to investigate changes in the signal-to-noise-ratio of climate-related changes in e.g., $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ when for example seasonal CO_2 changes in the cave air occur or to study the effect of different CaCO_3 sampling strategies for isotope measurements, which can smooth the original $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signal in dependence on the growth rate (Baldini et al., 2008a).

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SUPPLEMENTARY MATERIAL

- 1) User manual
- 2) ISOLUTION model code V1.0 for MATLAB

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