

# PHYSICS AND CHEMISTRY OF CO<sub>2</sub> OUTGASSING FROM A SOLUTION PRECIPITATING CALCITE TO A SPELEOTHEM: IMPLICATION TO <sup>13</sup>C, <sup>18</sup>O, AND CLUMPED <sup>13</sup>C<sup>18</sup>O ISOTOPE COMPOSITION IN DIC AND CALCITE

## FIZIKA IN KEMIJA RAZPLINJANJA CO<sub>2</sub> PRI ODLAGANJU SIGE, S POSEBNIM OZIROM NA SIGNALE IZOTOPA <sup>18</sup>O IN IZOTOPSKEGA SKUPKA <sup>13</sup>C<sup>18</sup>O V RAZTOPLJENEM ORGANSKEM OGLJIKU IN KALCITU

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### Abstract

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**Wolfgang Dreybrodt: Physics and chemistry of CO<sub>2</sub> outgassing from a solution precipitating calcite to a speleothem: Implication to <sup>13</sup>C, <sup>18</sup>O, and clumped <sup>13</sup>C<sup>18</sup>O isotope composition in DIC and calcite**

Outgassing of CO<sub>2</sub> from thin water layers of a solution of CaCO<sub>3</sub> in an H<sub>2</sub>O-CO<sub>2</sub> system plays a crucial role in the precipitation of calcite. Understanding the process of outgassing of CO<sub>2</sub> during precipitation of calcite to the surface of stalagmites is important for the interpretation of isotope signals in the calcite deposited to the speleothem. There is, however, some confusion in the literature about the physics and chemistry of this process. Indistinct terms like *forced*, *enhanced*, *rapid*, *intense*, *slow*, *increased*, *equilibrium* and *progressive outgassing* are used widely in the literature to explain the impact on isotope composition of the calcite deposited. It is shown that in all the variety of conditions occurring in nature only two distinct processes of outgassing exist. 1. Diffusion controlled outgassing: In the first step, whenever a thin water layer of calcareous solution is present, either on the cave wall or on the surface of a stalagmite, molecular CO<sub>2</sub> escapes within several seconds by physical diffusion and after about 40 seconds pH and DIC in the solution achieve chemical equilibrium with respect to the CO<sub>2</sub> in the cave atmosphere. 2.) Controlled by precipitation: In the second step this supersaturated solution precipitates calcite, whereby for each unit CaCO<sub>3</sub> deposited one molecule of CO<sub>2</sub> is generated and escapes from the solution by molecular diffusion. This precipitation controlled outgassing is active during precipitation only. All variations of outgassing mentioned in the literature can be explained

### Izvleček

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**Wolfgang Dreybrodt: Fizika in kemija razplinjanja CO<sub>2</sub> pri odlaganju sige, s posebnim ozirom na signale izotopa <sup>18</sup>O in izotopskega skupka <sup>13</sup>C<sup>18</sup>O v raztopljenem organskem ogljiku in kalcitu**

Razplinjanje CO<sub>2</sub> iz tanke plasti raztopine sistema CaCO<sub>3</sub> in H<sub>2</sub>O-CO<sub>2</sub> je pomembno za izločanje kalcita in interpretacijo izotopskih signalov v odloženem kalcitu. V literaturi je precejšnja zmeda pri obravnavanju fizike in kemije procesa razplinjanja, saj raziskovalci uporabljajo različne izraze, kot so *prisiljeno*, *poudarjeno*, *počasno*, *povečano* in *progresivno* razplinjanje. V članku pokažem, da sta pri vseh različnih razmerah v naravi bistvena le dva procesa razplinjanja. 1) Difuzijsko razplinjanje: v prvem koraku molekularni CO<sub>2</sub> v nekaj sekundah z difuzijo preide iz tanke plasti vode, ki polzi ali po jamski steni ali po površini sige. Po približno 40 sekundah pH in raztopljeni organski ogljik v raztopini dosežeta ravnovesje z atmosferskim CO<sub>2</sub>. 2) Razplinjanje pri izločanju: v drugem koraku prenasočena raztopina izloča kalcit, pri čemer se za vsako odloženo molekulo CaCO<sub>3</sub> iz raztopine sprostijo molekula CO<sub>2</sub>, ki potem z difuzijo uide v jamsko atmosfero. S tega procesa lahko pojasnimo vse druge načine razplinjanja, ki jih omenja literatura. Nato pokažem, da CO<sub>2</sub>, ki se razplini v prvem koraku, ne vpliva na izotopsko sestavo zaloge HCO<sub>3</sub><sup>-</sup> v raztopini in zato tudi v izločenem kalcitu. Izotopska sestava HCO<sub>3</sub><sup>-</sup> je tako za <sup>13</sup>C in za <sup>18</sup>O povsem določena z razplinjanjem med izločanjem kalcita. Ujemanje količine razplinjenega CO<sub>2</sub> in izločenega kalcita pokažem tudi s poskusom. Rezultati omogočajo kritično obravnavo uporabe termometra na osnovi

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by one of these two types of outgassing. Furthermore it is shown that the first step of outgassing driven by diffusion has no influence on the isotope composition of the  $\text{HCO}_3^-$  reservoir in the solution and consequently on that of calcite precipitated from it. The isotope composition of  $\text{HCO}_3^-$  for  $^{13}\text{C}$  as well as for  $^{18}\text{O}$  solely is determined by the second step of precipitation controlled outgassing. An experiment is presented proving that the amount of  $\text{CO}_2$  escaping from the solution during precipitation of calcite at any time is equal to the amount of calcite precipitated. The results are used for a critical application to the  $\Delta_{47}$  clumped isotope thermometer that explains why in most stalagmites the calcite is not a good candidate to obtain correct temperatures at the time of its deposition.

**Key words:** isotope, clumped isotope, speleothem, calcite, paleo-thermometer.

izotopskega skupka  $\Delta_{47}$  in pojasnjujejo, zakaj kalcit ni primeren za določanje temperature v času izločanja..

**Ključne besede:** izotop, izotopski skupek, siga, kalcit, paleo temperatura.

## INTRODUCTION

Outgassing of  $\text{CO}_2$  from thin water layers containing a solution of  $\text{CaCO}_3$  in a water- $\text{CO}_2$  system plays a crucial role in the precipitation of calcite. During deposition of calcite from thin water layers, as they occur on stalagmites, two different processes of  $\text{CO}_2$  outgassing are active. First, when a calcareous solution drips to the stalagmite, aqueous  $\text{CO}_2$  escapes from the water film by molecular diffusion into the cave atmosphere with low  $p_{\text{CO}_2}$  until chemical equilibrium between the  $\text{CO}_2$  in the solution and that in the atmosphere is established. In chemical equilibrium the concentration,  $c_{\text{eq}}^{\text{CO}_2}$ , of aqueous  $\text{CO}_2$  in the water is related to the partial pressure,  $p_{\text{CO}_2}^{\text{cave}}$ , of  $\text{CO}_2$  in the cave by Henry's law,  $c_{\text{eq}}^{\text{CO}_2} = K_{\text{H}} \cdot p_{\text{CO}_2}^{\text{cave}}$ , where  $K_{\text{H}}$  is Henry's constant. For water layers with a depth,  $\delta$ , of several tenths of a millimeter this process is fast and takes about ten seconds in agreement to the theoretically predicted exponential time constant,  $\tau_{\text{diff}} = 4\delta^2/(\pi^2 D)$ , where  $D = 2 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  is the diffusion constant of aqueous  $\text{CO}_2$  (Dreybrodt 1988; Dreybrodt 2011; Hansen *et al.* 2013). Note that the time constant,  $\tau_{\text{diff}}$  for outgassing is independent of the difference between the  $p_{\text{CO}_2}$  in the solution and the  $p_{\text{CO}_2}$  in the cave atmosphere. During this first step of diffusive outgassing of dissolved molecular  $\text{CO}_2$  the solution remains undersaturated and calcite cannot be precipitated. Therefore, the  $\text{Ca}^{2+}$ -concentration remains constant. The  $\text{HCO}_3^-$  concentration remains constant also because it is tied to the  $\text{Ca}^{2+}$ -concentration by electro neutrality.

After outgassing is completed the concentration of  $\text{H}_2\text{CO}_3$  is reduced also. Therefore pH rises and the concentrations  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  are no longer in equilibrium with respect to the lower concentration of  $\text{CO}_2$  in the solution. Establishing chemical equilibrium needs the time,  $\tau_{\text{eq}}$ , of about 40 s, independent of the depth,  $\delta$ ,

of the water layer (Hansen *et al.* 2013) and causes supersaturation with respect to calcite. The pH-value after completion of this process is above 8. These processes have been explored experimentally (Hansen *et al.* 2013).

After establishment of supersaturation calcite is precipitated to the surface of the stalagmite until after the time  $3\tau_{\text{prec}}$ , 95% of the calcite is precipitated and equilibrium with respect to calcite is obtained. During precipitation, stoichiometry of the reaction  $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$  requires that for each molecule of  $\text{CaCO}_3$  deposited one molecule of  $\text{CO}_2$  must be released into the solution from where it outgasses by molecular diffusion into the surrounding atmosphere. This second step of outgassing is controlled by calcite precipitation, which releases  $\text{CO}_2$  molecules into the water. These escape from the solution by molecular diffusion and the amount of  $\text{CO}_2$  released into the atmosphere is equal to the amount of calcium withdrawn from the solution by precipitation into calcite.

These two different types of outgassing have caused confusion in the speleothem research community. Indistinct terms like *forced, enhanced, rapid, intense, slow, fast, minimal, increased, equilibrium and progressive outgassing* are scattered throughout the literature without clear definitions of their meaning. In a large number of papers the term outgas or degas is used this way many times. As an example, the book "Speleothem Science" referencing the current literature (Fairchild & Baker 2012) uses the term "degas" 148 times, but does not give a clear description of its meaning. In a similar way the term degas is used in a recent paper 90 times (Mickler *et al.* 2019).

There is consensus in the scientific community that understanding of the physics and the chemistry in cave

processes is of utmost importance to decipher paleo-climatic information from time series of <sup>18</sup>O and <sup>13</sup>C signals recovered from stalagmites. In this paper I discuss the processes of outgassing of CO<sub>2</sub> from thin water layers on

the top of a stalagmite. In addition I present an experiment elucidating that outgassing related to precipitation of calcite is controlled by precipitation and ceases when precipitation stops.

## MATERIALS AND METHODS

### H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub> SOLUTIONS

In order to study chemical equilibration and precipitation of calcite in a batch experiment, we prepared a supersaturated H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub> solution with Milli-Q water in a 5 L-Duran borosilicate glass vessel. To get the desired concentration of Ca<sup>2+</sup> the corresponding amount of Baker analyzed CaCO<sub>3</sub> was added to the water and stirred with a magnetic mixer. Subsequently, the solution was sparged with high purity CO<sub>2</sub>-4.5 (Linde). After a few hours, the solution becomes clear and translucent indicating complete dissolution of CaCO<sub>3</sub>. To obtain a solution slightly supersaturated with respect to calcite nitrogen is bubbled through the solution until pH of about 7 is established. This solution can be kept in the bottle for several days without changing pH and Ca<sup>2+</sup> concentration. (Hansen *et al.* 2013).

As can be calculated by PHREEQC2 (Parkhurst and Appelo 1999), the specific conductivity of the solution,  $\sigma$ , is linearly related to its Ca<sup>2+</sup> concentration,  $c$ . For pH  $\cong$  8 and Ca<sup>2+</sup> concentrations between 1 and 8 mmol/L at a temperature of 25 °C, one finds experimentally the relation  $\sigma = 60 + 153c$  between specific conductivity,  $\sigma$  ( $\mu$ S/cm), and Ca<sup>2+</sup> concentration,  $c$ , in mmol/L (Hansen *et al.* 2013).

### EXPERIMENTAL SET-UP

Fig. 1 shows the experimental set up. A box with a volume of 67 L closed to the outside atmosphere contains a beaker with 0.7 L of the solution that is stirred by a magnetic stirrer. A membrane pump bubbles the air in the box through this solution from where it turns back to the atmosphere in the box. The specific conductivity of the solution is measured with a Mettler-Toledo® InLab®738 Conductivity Probe. The CO<sub>2</sub> concentration in the box is monitored during the experiment using a Vaisala® CO<sub>2</sub>-sensor. Prior to the experiment, the box is flushed with pure N<sub>2</sub> or Ar until CO<sub>2</sub> was zero. Then 67ml of CO<sub>2</sub> are injected by a syringe to obtain a  $p_{\text{CO}_2} = 10^{-3}$  atm. After several hours the solution was in equilibrium with the surrounding  $p_{\text{CO}_2}$  in the box. To initiate precipitation of calcite 2.5g of calcite seed crystals (Baker analysed) are added to the supersaturated solution through a funnel. Precipitation of calcite to the surface of the seed crystals starts immediately. The temporal evolution of electrical conductivity and  $p_{\text{CO}_2}$  is measured until no further change occurred. The experiment was performed at ambient temperature of 25°C that was constant within 0.5°C during the experiment.

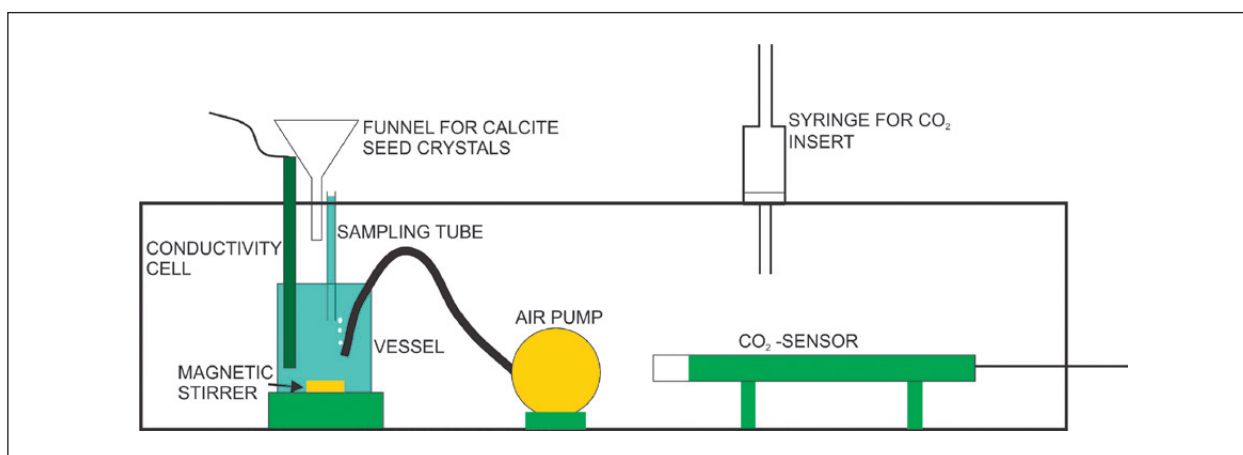


Fig. 1: Experimental set up.

EXPERIMENTAL RESULTS

Fig. 2 depicts the temporal evolution of the total amount of CO<sub>2</sub> in the atmosphere in the box and the total amount of calcium in the solution. Both curves show an expo-

ponential approach to equilibrium. The exponential times within the limit of error of about 5% are equal. Figure 3 illustrates the amount of CO<sub>2</sub> released from the solution

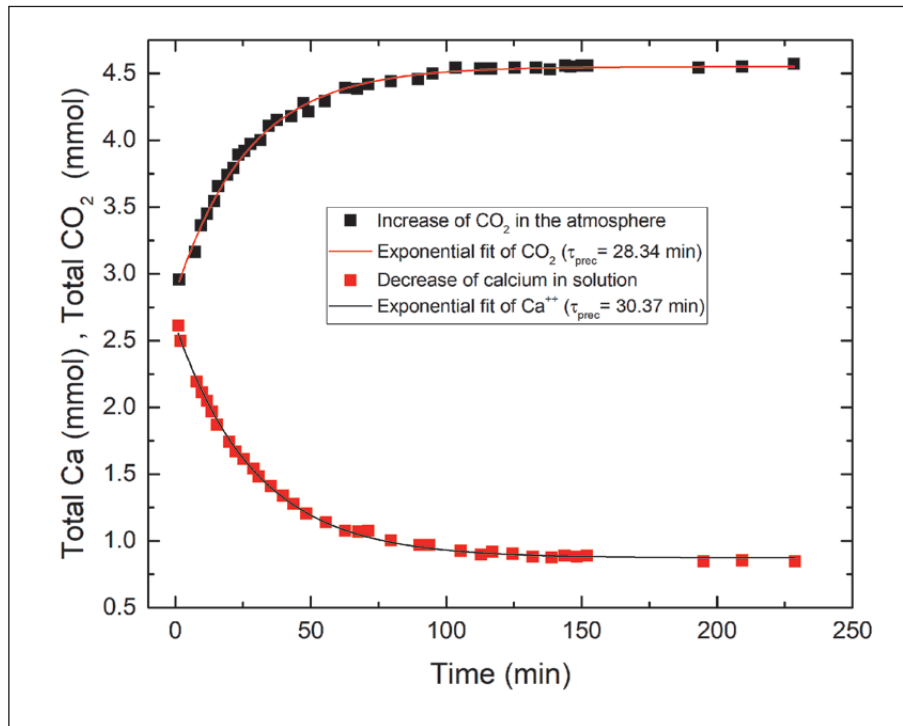


Fig. 2: Temporal evolution of the amount of CO<sub>2</sub> contained in the atmosphere in the box and the amount of Ca contained in the solution.

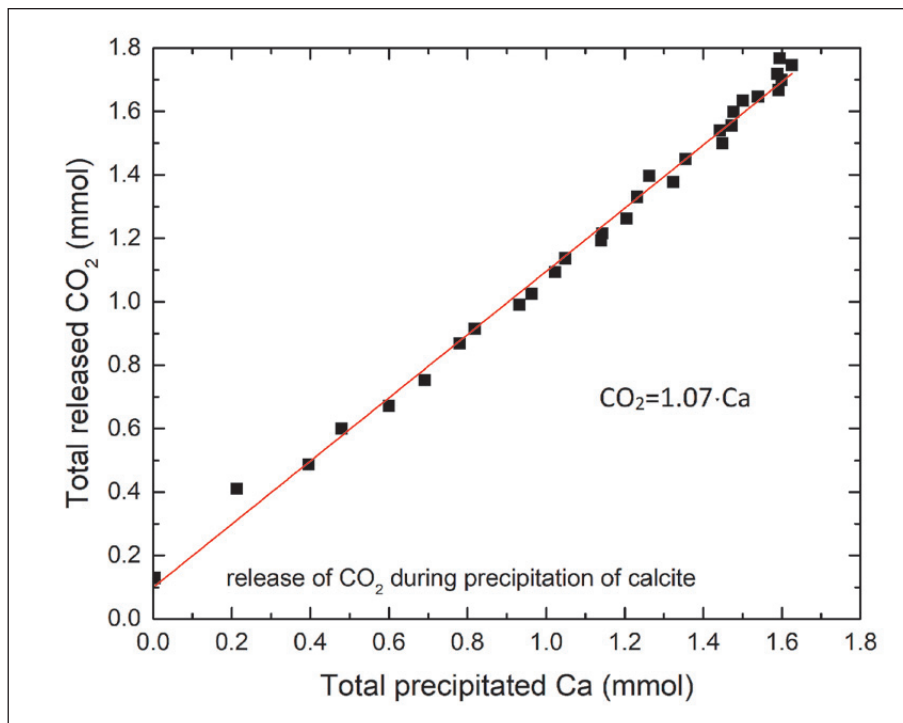


Fig. 3: Amount of CO<sub>2</sub> released into the atmosphere versus the amount of Ca precipitated from the solution.

during precipitation of calcite versus the amount of calcium removed from the solution by precipitation. As one can see from the straight line with slope 1, the amount of

CO<sub>2</sub> released is equal to the amount of CaCO<sub>3</sub> precipitated during the entire experiment.

## DISCUSSION

The two different processes of outgassing are both limited in time.

1) Outgassing by molecular diffusion into the atmosphere depends on the depth of the water layer,  $\delta$ , by  $\tau_{\text{diff}} = 4\delta^2/(\pi^2D)$ . For water layers with depth as they are common on speleothems one finds times,  $\tau_{\text{diff}}$ , of outgassing between 2 s up to 32 s for 0.01 cm  $< \delta < 0.04$  cm.

(2) Outgassing controlled by precipitation of calcite proceeds with exponential precipitation time constant,  $\tau_{\text{prec}} = \delta/\alpha$ .  $\alpha$  is the kinetic rate constant of the rate law for precipitation,  $R = \alpha(c - c_{\text{eq}})$ , where  $c$  in mol cm<sup>-3</sup> is the calcium concentration in the water layer,  $c_{\text{eq}}$  the equilibrium concentration of calcium with respect to the  $p_{\text{CO}_2}$  (atm) in the cave atmosphere and with respect to calcite (Buhmann and Dreybrodt 1985; Dreybrodt 1988). The kinetic constant depends on temperature by the relation  $\alpha = (0.52 + 0.04T + 0.004T^2) \cdot 10^{-5}$  cm/s and increases by about a factor of ten from 0°C to 25°C.  $T$  is temperature in °C. (Baker *et al.* 1998). With these data precipitation times range between 2000 s and 250 s for  $\delta = 0.01$  cm at  $T = 0^\circ\text{C}$  and  $25^\circ\text{C}$ , respectively. For all temperatures  $\tau_{\text{prec}}$  is larger than  $\tau_{\text{diff}}$  by one order of magnitude.

If the drip intervals  $T_{\text{drip}} \ll \tau_{\text{diff}} + \tau_{\text{eq}}$  the residence time of the water on top the stalagmite will be short and there may not be sufficient time for the solution to outgas and to become supersaturated with respect to calcite (provided this has not happened by prior calcite precipitation on the cave walls) and consequently precipitation of calcite is not active. This means that during fast dripping,  $T_{\text{drip}} \ll \tau_{\text{diff}} + \tau_{\text{eq}}$  stalagmites may exhibit a hiatus at the apex. Calcite precipitation starts after supersaturation has been attained. It ceases after

the time  $3 \cdot \tau_{\text{prec}}$  during which 95% of the calcite available have been deposited. Therefore isotope signals imprinted for drip times  $T_{\text{drip}} > 3 \cdot \tau_{\text{prec}} + \tau_{\text{diff}} + \tau_{\text{eq}}$  will all be independent of drip time. Only for  $T_{\text{drip}} < 3 \cdot \tau_{\text{prec}} + \tau_{\text{diff}} + \tau_{\text{eq}}$  the isotope signal in the calcite does depend on drip time, because for times larger than  $3 \cdot \tau_{\text{prec}}$ , 95% of the calcite is deposited and further precipitation of the remaining 5% has no significant impact (Dreybrodt 2011; Dreybrodt 2016). It may be instructive to consider the amounts of CO<sub>2</sub> outgassing during the two steps of outgassing. Using the program EQUILIBRIUM (Dreybrodt 1988), updated by F. Gabrovšek, I find the following numbers.

When the water enters into the cave, calcium concentrations of about 2 mmol/L and CO<sub>2</sub> concentrations in the solution of about 0.5 mmol/L are common. After outgassing by diffusion into a cave atmosphere with  $p_{\text{CO}_2}$  of 0.0004 atm these solutions contain 2 mmol/L of calcium but only about 0.02 mmol/L of aqueous CO<sub>2</sub>. Thus typical amounts of CO<sub>2</sub> lost from the solutions in the first step by diffusion is about 0.48 mmol/L. In the second step of precipitation controlled outgassing, the calcium concentration changes from 2 mmol/L to 0.63 mmol/L. The corresponding amount of CO<sub>2</sub> lost during precipitation is therefore 1.37 mmol/L. This is about three times more than what is lost during the first step of diffusion driven outgassing.

Within this concepts of outgassing there is no need to consider forced, enhanced, rapid, intense, slow, increased, equilibrium, or progressive outgassing as relevant processes. They all can be defined either by diffusion controlled or by precipitation controlled outgassing.

The influence of  $p_{\text{CO}_2}$  in the cave atmosphere to the isotope composition of calcite is often discussed in the

$P_{\text{CO}_2}$ in cave atmosphere atm	$C_{\text{eq}}$ mmol/L	Precipitation rate, R, for $c_{\text{in}} = 2$ mmol/L mmol cm <sup>-2</sup> s <sup>-1</sup>
$3.5 \cdot 10^{-4}$	0.64	$1.70 \cdot 10^{-8}$
$2 \cdot 10^{-3}$	1.17	$1.04 \cdot 10^{-8}$
$5 \cdot 10^{-3}$	1.62	$4.75 \cdot 10^{-9}$
$8 \cdot 10^{-3}$	1.92	$1.00 \cdot 10^{-9}$
$1 \cdot 10^{-2}$	2.07	$-8.75 \cdot 10^{-10}$

Tab. 1: Equilibrium concentration of Ca with respect to calcite and precipitation rates in dependence on partial pressure,  $p_{\text{CO}_2}$  of CO<sub>2</sub> in the cave atmosphere.  $c_{\text{in}} = 2$  mmol/L,  $T = 10^\circ\text{C}$ .



literature in terms of outgassing rates associated with the  $p_{\text{CO}_2}$  difference (gradient) between solution and the cave atmosphere. In this sense rates are called enhanced, when  $p_{\text{CO}_2}$  in the cave is low. This, however, has no impact on the isotope composition of the calcite deposited for the following reasons.

A change of  $p_{\text{CO}_2}$  causes a change of,  $c_{\text{eq}}$ , the equilibrium concentration of calcium by the relation  $c_{\text{eq}} = k \cdot \sqrt[3]{p_{\text{CO}_2}}$  where  $k$  is a constant depending on temperature (Dreybrodt 1988).  $c_{\text{eq}}$  is listed in Tab. 1 for various  $p_{\text{CO}_2}$  at a temperature of 10°C. For a solution impinging to the stalagmite with concentration,  $c_{\text{in}} = 2 \text{ mmol/L}$ , using the rate law for calcite deposition,  $R = \alpha(c_{\text{in}} - c_{\text{eq}})$ , (Buhmann & Dreybrodt 1985; Dreybrodt 1988) and employing  $\alpha = 1.25 \cdot 10^{-5} \text{ cm/s}$  at 10°C one finds the initial precipitation rates as listed in Tab. 1.

Precipitation rates decrease with increasing  $p_{\text{CO}_2}$  and at  $p_{\text{CO}_2} > 0.01 \text{ atm}$  the solution becomes corrosive. The corresponding rates of  $\text{CO}_2$  outgassing controlled by calcite precipitation are equal to the withdrawal rates of calcium from the solution by precipitation of calcite. During precipitation of calcite outgassing is determined by the precipitation rates and not by  $p_{\text{CO}_2}$  difference (gradient) between solution and cave atmosphere.

At that point it is important to realize that only outgassing controlled by precipitation has an impact on the isotope composition of both  $^{13}\text{C}$  as well as  $^{18}\text{O}$  in  $\text{HCO}_3^-$  in the solution and consequently to the calcite precipitated. Equilibration of  $^{18}\text{O}$  in  $\text{HCO}_3^-$  with water proceeds on time scales of several thousand seconds (Beck 2004) and can be neglected during the short time scales considered here.

For  $\text{pH} < 8.3$  there are two large reservoirs of carbon:  $\text{HCO}_3^-$  dominant for  $\text{pH} > 7.5$  and aqueous  $\text{CO}_2$  dominant for  $\text{pH} < 6$ . Water entering into the cave with 2 mmol/L of calcium exhibits a pH of about 7.3 with 4 mmol/L of  $\text{HCO}_3^-$  and 0.5 mmol/L aqueous  $\text{CO}_2$ . The first step of diffusion controlled outgassing of  $\text{CO}_2$  takes about 10 s. During this time the reservoir of  $\text{HCO}_3^-$  remains unaffected as electro neutrality requires  $c_{\text{HCO}_3^-} = 2 \cdot c_{\text{Ca}}$  and calcite has not yet been removed by precipitation.

The reservoir of aqueous  $\text{CO}_2$  is depleted to 0.02 mmol/L. After this first step of outgassing pH rises to 8.25 and precipitation starts. Since diffusive outgassing of aqueous  $\text{CO}_2$  is accomplished by molecular diffusion of two non interacting independent species, the heavy and the light isotope, isotope equilibrium between the gas and the aqueous  $\text{CO}_2$  is attained after the short time of  $\tau_{\text{diff}}$ .

Subsequently the reservoir of  $\text{HCO}_3^-$  approaches chemical and isotope equilibrium on the order of several 10 s (Zeebe *et al.* 1999). During equilibration the concentrations  $c_{\text{HCO}_3^-}$  and  $c_{\text{CO}_2}$  remain constant.  $c_{\text{CO}_2}$  is fixed

due to the constant  $p_{\text{CO}_2}$  in the cave atmosphere and the concentration of  $\text{HCO}_3^-$  is tied to the calcium concentration,  $c_{\text{Ca}}$ , by electro neutrality,  $c_{\text{HCO}_3^-} = 2 \cdot c_{\text{Ca}}$ , at pH about 8. During the time of equilibration the system is closed. Neither calcium and  $\text{HCO}_3^-$  nor  $\text{CO}_2$  are removed from the solution. Therefore,  $\delta_{\text{DIC}}$ , must remain constant. After outgassing one has

$$\delta_{\text{DIC}}^{\text{out}} = \frac{c_{\text{HCO}_3^-} \cdot \delta_{\text{HCO}_3^-}^{\text{out}} + c_{\text{CO}_2} \cdot \delta_{\text{CO}_2}^{\text{out}}}{(c_{\text{HCO}_3^-} + c_{\text{CO}_2})} \quad (1)$$

After equilibration  $\delta_{\text{DIC}}^{\text{eq}}$  is given by

$$\delta_{\text{DIC}}^{\text{eq}} = \frac{c_{\text{HCO}_3^-} \cdot \delta_{\text{HCO}_3^-}^{\text{eq}} + c_{\text{CO}_2} \cdot \delta_{\text{CO}_2}^{\text{eq}}}{(c_{\text{HCO}_3^-} + c_{\text{CO}_2})} \quad (2)$$

Equating both one obtains the change in  $\Delta\delta_{\text{HCO}_3^-}$  as

$$\Delta\delta_{\text{HCO}_3^-} = \delta_{\text{HCO}_3^-}^{\text{eq}} - \delta_{\text{HCO}_3^-}^{\text{out}} = \frac{c_{\text{CO}_2}}{c_{\text{HCO}_3^-}} (\delta_{\text{CO}_2}^{\text{out}} - \delta_{\text{CO}_2}^{\text{eq}}) \quad (3)$$

The isotope composition of aqueous  $\text{CO}_2$  in any case is determined solely by that of the  $\text{CO}_2$  in the cave atmosphere. As the isotope composition of  $\text{CO}_2$  in the atmosphere does not change during outgassing and equilibration,  $\delta_{\text{CO}_2}^{\text{out}} = \delta_{\text{CO}_2}^{\text{eq}}$ . Therefore, according to eqn.3,  $\Delta\delta_{\text{HCO}_3^-} = 0$ . The only reaction between carbon in  $\text{CO}_2$  in the solution and in the cave atmosphere and carbon in the carbonate reservoir so far not considered is isotope exchange. This reaction, however, is slow on the order of several 1000 s; Dreybrodt & Romanov 2016; Dreybrodt *et al.* 2016 ) and can safely be neglected.

These arguments are in agreement with observations of Spötl *et al.* (2005). In a cave monitoring campaign during 4 years they have measured the isotope compositions  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in the cave atmosphere and that of DIC in drip water that was outgassed after collection, exhibiting pH above 8.  $p_{\text{CO}_2}$  changes seasonally from 1400 ppm in summer to 400 ppm in winter.  $^{13}\text{C}$   $\delta_{\text{CO}_2}^{\text{atm}}$  is about -20‰ in summer and -15‰ in winter. Drip water DIC exhibits  $\delta$ -values  $^{13}\text{C}$   $\delta_{\text{HCO}_3^-}^{\text{eq}} = -11‰$  in summer and -8‰ in winter, respectively. All  $\delta$ -values are in VPDB.

Using  $\delta_{\text{CO}_2}^{\text{out}} = ^{13}\text{C}$   $\delta_{\text{CO}_2}^{\text{atm}} - \epsilon_{\text{CO}_2.\text{gas}/\text{CO}_2.\text{sol}}$ ,  $\delta_{\text{CO}_2}^{\text{eq}} = ^{13}\text{C}$   $\delta_{\text{HCO}_3^-}^{\text{eq}} - \epsilon_{\text{HCO}_3^-/\text{CO}_2.\text{gas}}$  with  $\epsilon_{\text{CO}_2.\text{gas}/\text{CO}_2.\text{sol}} = 1.1‰$ ,  $\epsilon_{\text{HCO}_3^-/\text{CO}_2.\text{gas}} = 11‰$  at 10°C (Mook 2000), and  $c_{\text{CO}_2} / c_{\text{HCO}_3^-} \cong 0.05$  at  $\text{pH} \cong 8$ , one gets  $\Delta\delta_{\text{HCO}_3^-}^{\text{summer}} \cong 0.05‰$  and  $\Delta\delta_{\text{HCO}_3^-}^{\text{winter}} \cong 0.15‰$ . These numbers show that the effect onto the isotope composition  $\text{HCO}_3^-$  reservoir by outgassing is small and can be regarded as zero within the limits of error of the measurement.

In all the processes discussed so far, it is only the mass difference between the light and heavy isotopes that causes changes in the isotope composition of the  $\text{HCO}_3^-$  pool. Therefore clumped isotopes must obey the same rules with the consequence that all arguments given

above apply also to clumped isotopes for all reactions between pools of differing carbonate species: CO<sub>2</sub> in the atmosphere, aqueous CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and calcite.

*In conclusion I state that the first step of outgassing has no influence to the isotope composition of the calcite precipitated. Terms like rapid or enhanced outgassing in the discussion of isotope imprints are therefore meaningless.*

This is in contrast to statements in the current literature, among many others, like:

*“Focusing on the processes at the stalagmite top, the disequilibrium can be related to the initial CO<sub>2</sub> degassing, that proceeds within <10 s and leaves the DIC significantly <sup>18</sup>O enriched until it is re-equilibrated by exchange with the water isotopes through hydration/dehydration of CO<sub>2</sub> at timescales of 6200 (25°C) to 126,000 s (0°C). ... An additional source of <sup>18</sup>O enrichment is the Rayleigh-type evolution of the DIC during carbonate precipitation” (Kluge et al. 2014).*

or

*“Carbonates grow on the top of stalagmites from a thin water film on the order of 100 μm (Dreybrodt 1980) which leads to fast degassing of the CO<sub>2</sub> -supersaturated drip water (within few seconds; e.g., Dreybrodt & Scholz 2011) and which causes an initial isotopic disequilibrium.” (Kluge et al. 2015)*

In the view of my arguments above, only two steps of outgassing must be regarded. During the first step because of the loss of aqueous CO<sub>2</sub> the isotope composition of DIC is affected. But the isotope composition of the HCO<sub>3</sub><sup>-</sup> reservoir that constitutes about 95% of DIC after completion of this first step of degassing, remains unchanged and in isotope equilibrium with water. Any offset from this isotope composition, either in carbon, oxygen or in the clumped isotope <sup>13</sup>C<sup>18</sup>O exclusively results from precipitation of calcite and the concomitant outgassing of the CO<sub>2</sub> generated and also from the deposition of carbonate into the calcite. Therefore isotope offsets δ<sup>18</sup>O and Δ<sub>47</sub> in calcite samples precipitated from CaCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O solutions to samples precipitated from solutions in isotope equilibrium arise and are correlated linearly (Guo 2008). The Δ<sub>47</sub> offset per 1 ‰ of δ<sup>18</sup>O is about -0.020 ‰. (Affek & Zaarur 2014). Theoretical calculations of Guo (2008) indicate a reduction of 0.0175–0.029‰ in Δ<sub>47</sub> for each 1‰ increase in δ<sup>18</sup>O. Both <sup>18</sup>O and <sup>13</sup>C<sup>18</sup>O return to equilibrium with water at the same rate (Affek 2013).

Only calcite precipitated from a solution with DIC in isotope equilibrium with the water that has not yet precipitated calcite already is therefore in isotope equilibrium and can serve as paleo-thermometer (Guo 2008; Affek 2012).

## IMPLICATIONS FOR THE CALCIUM CARBONATE CLUMPED ISOTOPE Δ<sub>47</sub> THERMOMETER

Many attempts have been taken to use samples of synthetic calcite, speleothems, tufa, and organically precipitated calcite to obtain a universal carbonate clumped isotope thermometer calibration (Kelson et al. 2017 and references therein). Some samples fit into this thermometer, others do not. Kelson et al. (2017) report on synthetic samples precipitated by degassing of a CaCO<sub>3</sub>-CO<sub>2</sub> solution. They found that repeating these experiments with addition of carbonic anhydrase that warrants isotope equilibrium with water did not change the results. This shows that their methods of precipitating calcite were suitable for calibration. Kluge et al. (2015) have synthesized calcite under controlled conditions in the lab and have found the temperature dependence of Δ<sub>47</sub> close to that predicted theoretically.

Other samples, however, show offsets from the expected equilibrium values and are not suitable as thermometer. As an example Kluge and Affek (2012) observed such offsets in stalagmites and calcite precipitated to watch glasses below drip sites in caves.

Δ<sub>47</sub> of tufa precipitated several hundred meters downstream from its spring exhibits a distinct offset from the equilibrium composition (Kato et al. 2019) because on its way downstream the solution may have undergone calcite precipitation. In contrast Δ<sub>47</sub> of travertine precipitated close to the vents of the springs and presumably with little prior precipitation of calcite is close to equilibrium (Kele 2015).

During calcite deposition to the surface of speleothems precipitation forced CO<sub>2</sub> degassing from a thin layer of solution causes isotopic disequilibrium in the HCO<sub>3</sub><sup>-</sup> reservoir. The CO<sub>2</sub> released by degassing becomes depleted in δ<sup>13</sup>C and δ<sup>18</sup>O and enriched in Δ<sub>47</sub>. The DIC thus undergoes δ<sup>13</sup>C and δ<sup>18</sup>O enrichment and Δ<sub>47</sub> is depleted.

As a consequence only samples from speleothems that have been precipitated from solutions with DIC in isotope equilibrium with the water that has not lost calcite by prior calcite precipitation before dripping to the speleothem, are suitable to obtain correct temperatures by the Δ<sub>47</sub> thermometer.

It is almost impossible to warrant these conditions for stalagmites where the calcite has been deposited in the far past. Therefore, speleothems may be not good candidates for the  $\Delta_{47}$  thermometer.

Only stalagmites with diameters of about 10 cm and growth rates of several 100  $\mu\text{m}/\text{year}$  are suitable candidates. They have grown with drip times,  $T_{\text{drip}} < 0.01 * \tau_{\text{prec}}$ , such short that the water that flows off has no time to change its Ca concentration by more than one percent. (Dreybrodt 1999). In addition these stalagmites should be selected in caves with high rock coverage that warrants sufficiently long percolation times of the water to obtain isotope equilibrium between the the water and DIC (Dreybrodt & Scholz 2011). Such conditions are unlikely for most stalagmites.

Affek *et al.* (2015) have shown that speleothem calcite in Soreq Cave (Israel) is precipitated out of isotopic equilibrium with the cave drip water in agreement to other investigations in the literature (e.g., Kluge & Affek 2012; Daeron *et al.* 2011; Affek & Zaarur 2014).

Synthetic calcite grown in the lab must be precipitated from  $\text{CaCO}_3$  -  $\text{CO}_2$  solutions under the following conditions. The solution must be kept at constant temperature and pH below 8.5 for a sufficiently long time to

obtain isotope equilibrium between DIC and  $\text{H}_2\text{O}$ . For temperatures above 25°C, 9 hours are safe. For lower temperatures at about 15°C 24 hours are acceptable and at 5°C the time is three days. (Beck 2004; Beck *et al.* 2005).

During precipitation of calcite the conductivity of the solution, which is proportional to the calcium concentration must be monitored. It should not decrease by more than 2% to avoid isotope offset in the carbonate reservoir. In stagnant solutions calcite should be taken from the walls of the container to avoid collection of calcite particles precipitated at the water surface under not well defined chemical conditions. It may be preferable to stir the solution to ensure carbonate precipitation under well defined conditions and to avoid precipitation at its surface. Such solutions with pH about 8 can be also used to precipitate calcite in a water layer flowing down an inclined glass plate (Hansen *et al.* 2013), which is analogue to calcite precipitation on the surface of stalagmites (Hansen *et al.* 2019). Short residence times of about 10 s of the solution can be obtained at flow velocities of 0.1 cm/s. Scratching off calcite from the glass plate in the region between the onset of precipitation and about a few cm downstream should deliver samples that have been deposited in isotope equilibrium with the water.

## CONCLUSION

Understanding the process of outgassing of  $\text{CO}_2$  during precipitation of calcite to the surface of stalagmites is important for the interpretation of isotope signals. There is, however, some confusion in the literature about the physics and chemistry of this process. I have shown that in all the variety of natural conditions only two distinct processes of outgassing exist. First, when the drop hits the surface of the stalagmite forming a thin film of solution molecular  $\text{CO}_2$  escapes by physical diffusion within several seconds and after about 40 seconds the solution achieves chemical equilibrium with respect to the  $\text{CO}_2$  in the cave atmosphere. This solution is supersaturated and precipitates calcite, whereby for each unit  $\text{CaCO}_3$

one molecule of  $\text{CO}_2$  is generated, which escapes by molecular diffusion from the solution into the atmosphere. This precipitation controlled outgassing is active during precipitation only and is controlled chemically. All variations of outgassing discussed in the literature can be explained by one of these two types of outgassing. Furthermore I show that the first step, outgassing driven by diffusion has no influence to the isotope composition of calcite for both,  $^{13}\text{C}$  and  $^{18}\text{O}$ , that is determined entirely by the second step of precipitation controlled outgassing.

The results are applied also to clumped isotopes  $^{18}\text{O}^{13}\text{C}$  and the consequences of their isotope evolution are discussed with regard to the  $\Delta_{47}$  thermometer.

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