

ISOTOPE EXCHANGE BETWEEN DIC IN A CALCITE DEPOSITING WATER LAYER AND THE CO₂ IN THE SURROUNDING ATMOSPHERE: RESOLVING A RECENT CONTROVERSY.

IZMENJAVA IZOTOPOV V RAZTOPLJENEM ANORGANSKEM OGLJIKU VODNE PLASTI, KI V ATMOSFERI S PRISOTNIM CO₂ IZLOČA KALCIT: POJASNILO PEREČIH NASPROTIJ

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INTRODUCTION

Time series of stable carbon and oxygen isotope values ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in stalagmite calcite are important paleoclimate proxies (Fairchild & Baker 2012). However, the isotope signal resulting from climatic variability is superimposed by isotope imprints resulting from physical and chemical processes during precipitation of speleothem calcite, which are independent of climate. Precipitation of calcite causes enrichment of the heavy isotopes for both oxygen and carbon in the DIC that depends on drip time, the calcium concentration in the drip water, but also on its temperature (Dreybrodt 2008; Dreybrodt & Scholz 2011).

If the CO₂ in the cave atmosphere is not in isotope equilibrium with the dissolved inorganic carbon (DIC) in the calcite depositing solution isotope exchange between both can add isotope imprints to the calcite deposited (Dreybrodt & Romanov 2016). To understand the origin of these signals helps in the interpretation of stalagmite time series.

In the case of isotope exchange the change in the δ -value of the DIC and in the calcite deposited from it during the drip interval T_{drip} is given by $\Delta_{\text{DIC}}(T_{\text{drip}}) \cong (\delta_{\text{eq}}^{\text{atm}} - \delta_0) T_{\text{drip}} / \tau_{\text{ex}}$, where $(\delta_{\text{eq}}^{\text{atm}} - \delta_0)$ is the difference between the initial δ -value, δ_0 , of the DIC and the value $\delta_{\text{eq}}^{\text{atm}}$ if DIC were in isotope equilibrium with the

CO₂ in atmosphere. τ_{ex} is the exchange time for the exponential approach to isotope equilibrium between the CO₂ in the cave atmosphere and the DIC. This is valid for $T_{\text{drip}} < 0.2\tau_{\text{prec}}$, the time of exponential decay of precipitation of calcite (Dreybrodt and Romanov, 2016). Therefore changes in the δ -value of about 1‰ are possible. A most important parameter, which must be known is the exchange time, τ_{ex} , because it determines the contribution of a non climatic signal. Because of cave ventilation $\delta_{\text{eq}}^{\text{atm}}$ can exhibit values between -11 ‰ and -8 ‰ VPDB for carbon and 2 ‰ to 9 ‰ for oxygen (Töchterle *et al.* 2017). To find the impact of this variation, knowledge of exchange times is of utmost importance.

Dreybrodt *et al.* (2016) and Dreybrodt and Romanov (2016) have derived an equation (eqn. 1 in this work) to calculate the exchange time for all cases relevant to deposition of calcite to stalagmites.

Recently Hansen *et al.* (2017) have suggested an alternative reaction-diffusion model that, especially for cave environments, predicts significantly smaller exchange times than those these authors calculated by using the approach of Dreybrodt *et al.* (2016), where they neglected the pH dependent contribution from the reaction $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ converting CO₂ into HCO₃⁻. They conclude: "For low $p\text{CO}_2$ (*i.e.*, between 500

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and 1000 ppmV), as observed in many cave systems, the time constants calculated by our model are shorter than estimated by an alternative approach. (Dreybrodt et al. 2016)."

To resolve this controversy, in this paper we will show that both models yield results close to each other if the pH-dependent rate constant k for conversion of CO_2 into HCO_3^- is used in both approaches.

Hansen *et al.* (2017), also provided a wealth of experimental data from that the exchange times can be extracted, but they missed to do so. Since the validity of a theory can be only verified by experiments the evaluation of these data is the key for its reliable predictions and must not be missed.

I have used their experimental data to obtain the exchange times for a variety of temperatures, DIC -concentrations, p_{CO_2} , and thickness of the water layer. The values determined from this procedure are in agreement to the theoretical predictions.

It is the purpose of this work to resolve a controversy, which could spread confusion to a well resolved issue.

THE THEORY OF DREYBRODT *et al.*

Dreybrodt *et al.* (2016) and Dreybrodt and Romanov (2016) have presented a theory of the exchange time for a water layer of depth, a , and have verified it by experiments.

τ_{ex} can be expressed by

$$\tau_{\text{ex}} = \frac{\frac{a^2}{D}}{\sqrt{\frac{ka^2}{D} \tanh\left(\sqrt{\frac{ka^2}{D}}\right)}} \cdot \frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{K_{\text{H}} \cdot p_{\text{CO}_2}} = \tau_{\text{red}}^{\text{ex}} \cdot \frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{K_{\text{H}} \cdot p_{\text{CO}_2}} \quad (1)$$

Here D is the constant of molecular diffusion for aqueous CO_2 and $k = (k_{+1} + k_{+4}[\text{OH}^-])$ is the combined reaction constant for the parallel reactions $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{HCO}_3^- + \text{H}^+$ and $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ converting CO_2 into HCO_3^- . $[\text{HCO}_3^-]$ is the concentration of bicarbonate and $[\text{CO}_3^{2-}]$ that of carbonate, p_{CO_2} is the partial pressure of CO_2 in the surrounding atmosphere, and K_{H} is Henry's constant. $\tau_{\text{red}}^{\text{ex}}$, called reduced exchange time, is an abbreviation to split the equation in a first part determined by the transport properties and into a second one representing the chemical composition of the solution.

For $\text{pH} > 8.2$, k becomes strongly dependent on pH and DIC is redistributed between HCO_3^- and CO_3^{2-} . Since CO_3^{2-} and HCO_3^- are converted into each other by fast protonation they are in chemical equilibrium and isotopic equilibrium and the redistribution of carbonate species does not affect τ_{ex} (Dreybrodt & Romanov 2016).

THE REACTION-DIFFUSION MODEL OF HANSEN *et al.*

Recently Hansen *et al.* (2017), published an alternative approach by employing a complete reaction-diffusion model describing carbon isotope exchange between gaseous CO_2 and the DIC in thin solution films, as first suggested by Zeebe and Wolf-Gladrow (2001). They compare their results to these of Dreybrodt *et al.* (2016), by using eqn. 1. But, instead of employing the combined constant k , in their calculations they use $k = k_{+1}$ neglecting the contribution of the second pH-dependent reaction (eqn. 25 in their work) in all calculations. Consequently for all cases with $\text{pH} > 8.5$ they find exchange times higher than those predicted correctly by their model. Although they discuss in length that the combined constant k should be used, they do not apply this in eqn.1 to verify it. This would have solved the problem and avoided a confusing contradiction, which was stressed in the abstract of their work: "For low p_{CO_2} (between 500 and 1000 ppmV, as for strongly ventilated caves), our time constants are substantially lower than those derived in a previous study,----"

pH DEPENDENCE OF THE RATE CONSTANT k AND CONSEQUENCES TO THE EXCHANGE TIME

The reaction $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{HCO}_3^- + \text{H}^+$ consists of two parallel pathways. The first is the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$ with rate constant k_{+1} , which is dominant for $\text{pH} < 8.2$. For $\text{pH} > 8$ the reaction $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ with rate constant k_{+4} takes over. (Zeebe & Wolf-Gladrow 1999, 2001). The total rate constant is given by

$$k = k_{+1} + k_{+4}[\text{OH}^-]. \quad (2)$$

The brackets $[]$ denote concentrations. The temperature dependence of the constants is given by Johnson (1982).

Fig.1 illustrates the values of k in dependence on temperature for various values of pH . Note that k depends only weakly on pH in the region between 7.5 to 8.25, but then the values rise steeply with increasing pH . To obtain the pH dependence of the exchange times k has to be introduced into the equation for the reduced exchange time

$$\tau_{\text{ex}}^{\text{red}} = \frac{\frac{a^2}{D}}{\sqrt{\frac{ka^2}{D} \tanh\left(\sqrt{\frac{ka^2}{D}}\right)}} \quad (3)$$

from which the exchange time is obtained by multiplying with $\left(\frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{K_{\text{H}} \cdot p_{\text{CO}_2}}\right)$.

D is the constant of molecular diffusion of aqueous CO_2 . Its dependence of D on temperature is given by Jähne *et al.* (1987).

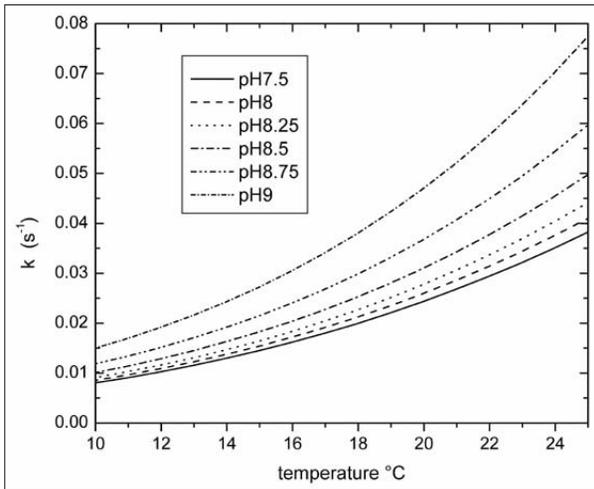


Fig. 1: Temperature dependence of the rate constant k of the reaction $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{HCO}_3^- + \text{H}^+$ for various values of pH.

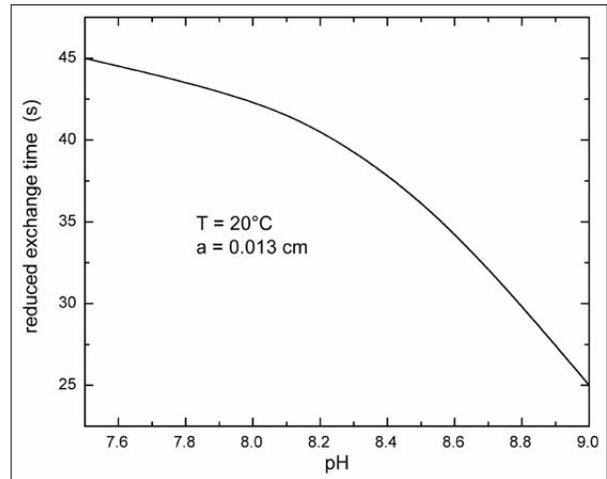


Fig. 3: Reduced exchange time as function of pH. Film depth $a = 0.013$ cm, $T = 20^\circ\text{C}$. From Dreybrodt and Romanov (2016).

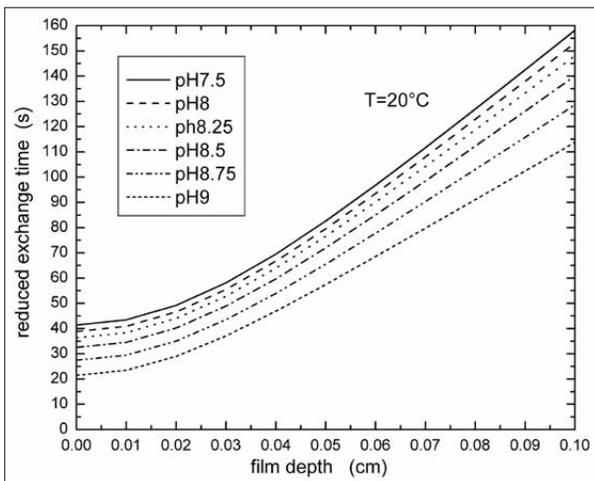


Fig. 2: Reduced exchange time $\tau_{\text{red}}^{\text{ex}}$ in dependence on film depth for various values of pH at a temperature of 20°C .

Fig. 2 shows the reduced exchange times, $\tau_{\text{red}}^{\text{ex}}$, as function of the depth, a , of the water layer for various pH. The region $0.01 \text{ cm} < a < 0.04 \text{ cm}$ is characteristic for water layers on the top of stalagmites. Fig. 3, already discussed in Dreybrodt and Romanov (2016), illustrates the pH dependence of $\tau_{\text{red}}^{\text{ex}}$ for a water layer with a depth of 0.013 cm at 20°C .

Dreybrodt *et al.* (2016) experimentally determined τ_{ex} for a water layer with depth, $a = 0.013 \text{ cm}$, containing 5 mmol/L NaHCO_3 in contact with an atmosphere with 500 ppm/V carbon dioxide. The pH of this solution calculated by using PHREEQC (Parkhurst & Apello 1999) is 8.73 . They found $\tau_{\text{red}}^{\text{ex}} = 29 \text{ s}$ in comparison to a value of 40 s at $\text{pH} = 8$, and 31 s for $\text{pH} = 8.73$ in Fig. 3. This provides evidence that the pH dependence of the exchange time has to be taken into account when considering iso-

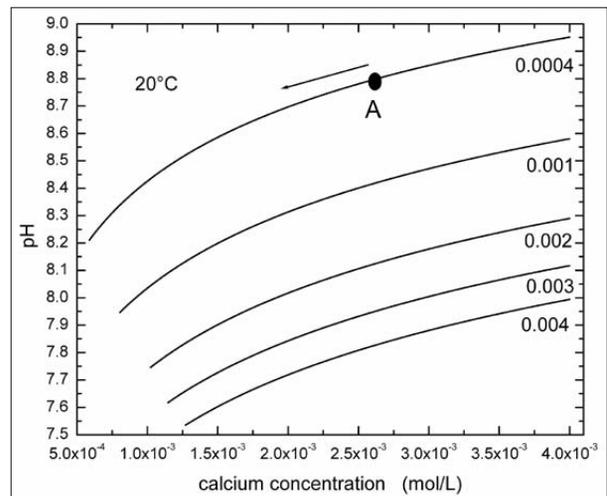


Fig. 4: pH of a calcite depositing $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ solution in dependence on the calcium concentration for various values of p_{CO_2} in the cave atmosphere given in atm at the corresponding curves. Note the drop in pH with increasing p_{CO_2} . From Dreybrodt and Romanov (2016).

tope exchange during precipitation of calcite on stalagmites, Dreybrodt and Romanov (2016).

To this end one needs to know the pH of the solution precipitating calcite to the stalagmite.

I have calculated the chemical composition of an $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ using an updated version of the program EQUILIBRIUM (Dreybrodt 1988) with Ca-concentration and p_{CO_2} as input parameters. The program is available on request. Fig. 4, see also Dreybrodt and Romanov (2016), shows the pH in the calcite precipitating water layer on top of the stalagmite as a function of Ca-concentration for p_{CO_2} values as they are common in caves. Each curve presents the evolution of pH when the

Tab. 1: Exchange times τ_{exp} determined from the experimental data of Hansen et al. (2017), in comparison to the values τ_{theo} derived by the model of Hansen et al. (2017). The lower part lists the results measured by Dreybrodt et al. (2016).

NaHCO_3 mmol/L	p_{CO_2} ppm	temperature °C	Depth of water mm	τ_{theo} s	τ_{exp} s
τ_{exp} determined from the experimental data of Hansen et al., 2017					
1	1000	10	0.12	2465	2820
2	1000	10	0.12	4725	4520
5	1000	10	0.12	10333	10060
10	1000	10	0.12	15769	20060
1	1000	20	0,14	1154	1600
2	1000	20	0,14	2189	2400
5	1000	20	0,14	4752	4400
10	1000	20	0,14	7876	6600
1	1000	30	0.13	670	1000
2	1000	30	0.13	1252	1860
5	1000	30	0.13	2613	2500
10	1000	30	0.13	4180	4000
1	3000	10	0.12	839	890
2	3000	10	0.12	1669	1976
5	3000	10	0.12	3999	3100
10	3000	10	0.12	7426	6100
1	3000	20	0.14	392	410
2	3000	20	0.14	778	1600
5	3000	20	0.14	1853	2000
10	3000	20	0.14	3414	3600
1	3000	30	0.13	233	260
2	3000	30	0.13	458	610
5	3000	30	0.13	1067	1200
10	3000	30	0.13	1914	1700
τ_{exp} determined experimentally by Dreybrodt et al., 2016					
5	25,000	room temp	0.6	556	570
10	25,000	room temp	0.6	1063	1110
5	12,500	room temp	0.6	1064	900
5	25,000	room temp	0.89	882	590
5	25,000	20	0.13	232	180
5	500	20	0.13	7739	7000
5	25,000	20	0.6	556	636
5	25,000	20	2	2753	2160

Ca-concentration decreases due to precipitation of calcite. For a given p_{CO_2} the initial Ca-concentration is represented by point A on the corresponding the curve. The evolution of pH during precipitation of calcite is then illustrated by the left-hand side of the curve designated by an arrow. For low $p_{\text{CO}_2} = 0.0004$ atm and initial Ca-concentration of 2 mmol/L, pH is 8.7. When precipitation stops pH has dropped to 8.2 at the left-hand side of

the curve. Therefore, at low p_{CO_2} , pH is high and the corresponding exchange times are low. For $p_{\text{CO}_2} > 0.002$ atm exchange times increase by a factor of about 1.4.

DETERMINATION OF τ_{ex} USING THE
EXPERIMENTAL DATA OF HANSEN *et al.*, 2017

Hansen *et al.* have also provided a wealth of experimental data on the early temporal evolution of $\delta^{13}\text{C}$ in a

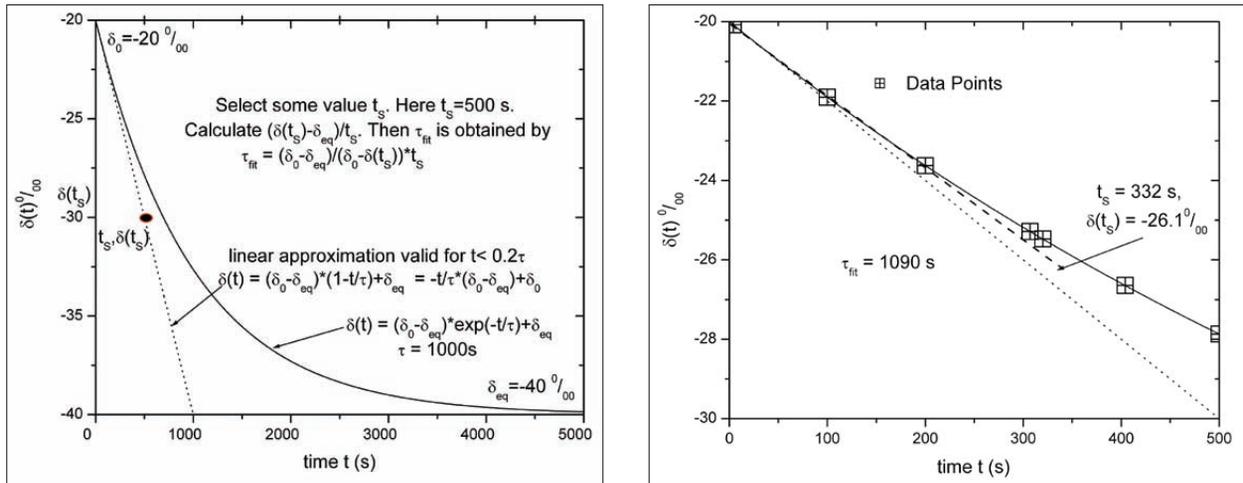


Fig. 5: a) Exponential approach to equilibrium (full line) in comparison to the linear approximation valid for $t < 0.2\tau$ (dotted line), b) Obtaining the exchange time τ from a set of experimental data points during the initial evolution where the linear approximation is valid. See text.

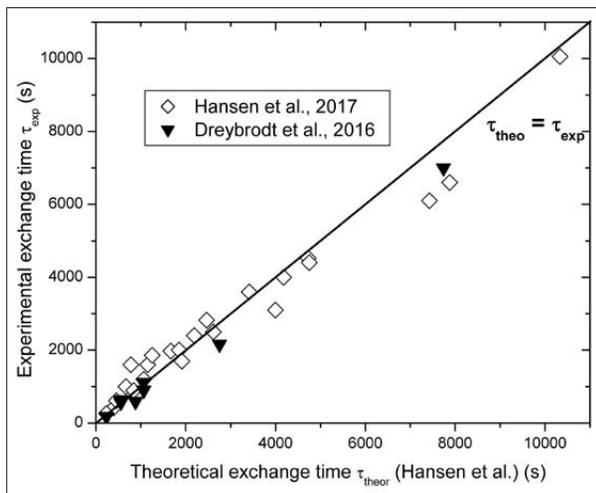


Fig. 6: Plot of experimental results versus theoretical prediction.

NaHCO₃ solution exposed up to 600 s to a defined CO₂ atmosphere. This reflects the early evolution, linear in time, of the exponential decay to an equilibrium value determined by the actual initial isotope composition of the CO₂ in the atmosphere. Hansen *et al.* state:

"Due to the relatively short exposure times on the plate (600 s at maximum), these experiments did not reach isotopic equilibrium. Most of the experimental data, thus, only show the initial part of the exponential evolution towards equilibrium (Fig. 7). The determination of a time constant for isotope exchange, τ_{ex} , according to Eq. (24) is, thus, not possible."

This statement is not correct and overlooks the approach of Dreybrodt *et al.* (2016), to determine initial experimental time constants of isotope exchange. It is possible to obtain the experimental time constants of

isotope exchange as has been shown already in this paper. Here we present the detailed procedure.

Fig. 5a illustrates the exponential approach to equilibrium by isotope exchange. The initial δ -value δ_0 of ¹³C in the DIC of the solution is supposed as -20 ‰ . Then the delta value approaches a value $\delta_{eq} = -40 \text{ ‰}$ in isotope equilibrium with the CO₂ in the atmosphere. This temporal evolution is given by

$$\delta(t) = (\delta_0 - \delta_{eq}) \exp(-t/\tau) + \delta_{eq} \quad (4)$$

For times $t < 0.2\tau$ using $\exp(-x) = 1-x$, $\delta(t)$ can be written as

$$\delta(t) = (\delta_0 - \delta_{eq}) \cdot (-t/\tau) + \delta_0 \quad (5)$$

This is depicted by the dotted straight line in Fig. 1a, which is almost identical to the exponential evolution for $t < 0.2\tau$. For any time t_s selected on the straight line one finds a corresponding value of $\delta(t_s)$ as given by eqn. 2. Solving for τ one gets

$$\tau = t_s (\delta_0 - \delta_{eq}) / (\delta_0 - \delta(t_s)) \quad (6)$$

Fig. 5b gives a series of data points as measured. To evaluate τ from them one fits the points up to $t = 200 \text{ s}$ by a straight line, which approximates the initial linear behavior. This is shown by the straight dashed line. For t_s we select the endpoint of this line to obtain $\tau = 1090 \text{ s}$, a value slightly higher than the real one. The upper full line presents the true exponential behavior whereas the dotted lower one shows its linear approximation. It is important to state here that knowledge of δ_{eq} is necessary. This is granted by the knowledge of the initial $\delta^{13}\text{CO}_2$ of the surrounding atmosphere. From this δ_{eq} can be obtained with sufficient accuracy by

$$\delta_{\text{eq}} = \delta^{13}\text{CO}_2 + \varepsilon_{\text{CO}_2/\text{HCO}_3} \quad (7)$$

where $\varepsilon_{\text{CO}_2/\text{HCO}_3}$ is the fractionation between CO_2 and HCO_3^- .

Using this method I have calculated the exchange times for all experimental data as provided by Hansen *et al.*, 2017, using their supplementary information. Due to the experimental errors in the data, e.g. Fig. 9 in Hansen *et al.* (2017), I crudely estimate an error of up to $\pm 20\%$, especially for large exchange times. Tab. 1 presents the results in comparison to their theoretical predic-

tions. I have also listed the results of the experiments of Dreybrodt *et al.* in comparison to the theoretical values of Hansen *et al.*

For a better overview, in Fig. 6, I have plotted the experimental values versus the theoretical predictions. For perfect agreement all these points should be located exactly on the line

$\tau_{\text{theo}} = \tau_{\text{exp}}$. All points are sufficiently close to this line and show a satisfactory agreement between theory and experiment.

CONCLUSION

In conclusion the work of Hansen *et al.* supports the prior theory of Dreybrodt *et al.*, 2016, and provides experimental evidence that the exchange times are predicted correctly by both approaches if the combined pH dependent rate constant k is used in both models. The statement of Hansen *et al.* (2017): "*For low p_{CO_2} (i.e., between 500 and 1000 ppmV), as observed in many cave systems, the time constants calculated by our model are shorter than estimated by an alternative approach (Dreybrodt *et al.*, 2016)*" is not correct. Both approaches yield numbers close to each other.

However, in the work of Hansen *et al.* (2017), the numerical procedure to obtain τ_{ex} requires a complex numerical program whereas eqn. 1 provides an analytical expression much easier to use, which expresses in a simple way the relation to p_{CO_2} and calcium concentration because electro neutrality requires $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 2[\text{Ca}^{2+}]$.

One remark should be added. Although, routinely the oxygen isotopes in the gaseous CO_2 as well as in the DIC are measured together with the carbon isotopes no information is given about them in the work of Hansen *et al.* (2017). As shown in Dreybrodt *et al.* (2016) these data can be obtained and give important supplementary information.

Hansen *et al.* (2017), have used CO_2 that was equilibrated with the water they used in their experiments. This way both CO_2 and DIC were in isotopic equilibrium with water and consequently also with each other. Consequently isotope exchange is excluded and the $\delta^{18}\text{O}$ values must stay constant during the time of the experiment. The evolution of $\delta^{18}\text{O}$ is reported in the bachelor thesis of Froeschmann (2015) and shows constant $\delta^{18}\text{O}$. This is what is expected and gives further support to the experimental method.

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