Note: ***The comments of Dr Defliese are in bold italics,*** the modification in the text are in red

- ***This paper by Thaler et al. is very well written, and I think would be of interest to a large number of people in the scientific community. The finding that disequilibrium precipitation can potentially be used to track 'true' equilibrium is novel, and potentially very exciting. I find the paper well written, and I have few comments or questions that the authors do not answer. My only general comment is that I caution the authors to not declare one set of d18O calibrations/measurement to be representative of equilibrium versus another as of this point. I (and probably many others in the community) am VERY sceptical of assertions that a single datapoint represents isotopic equilibrium for d18O and that all others do not. Overall, this is a good paper and I'm interested to see where this goes next.***

We would like to thank Dr William Defliese for accepting to review our work and for his encouraging comments. We are pleased that he found our article well written and our scientific finding to be novel and promising. Dr Defliese raised some comments to which we answered both in this letter and by modifying the text of the manuscript. We hope it improved the clarity of the manuscript.

- ***Abstract: Good Introduction: Good***
- ***My only general comment is that I caution the authors to not declare one set of d18O calibrations/measurement to be representative of equilibrium versus another as of this point. I (and probably many others in the community) am VERY sceptical of assertions that a single datapoint represents isotopic equilibrium for d18O and that all others do not.***
- ***Section 3.6: I'm not sure you can really make any statements here about better matching the Coplen (2007) and Watkins et al. (2013) data at low temperature, as figure 5 does not show error bars. When the errors are plotted (particularly important for the D47-based temperatures), it looks to me like your data overlaps both d18O calibration relationship.***

-We fully agree with Dr Defliese on this point. We regret that our manuscript could give the impression that we chose some calibrations as establishing the "true" equilibrium value. In order to deliver a much clearer message on this point, we modified the manuscript as follows:

Line 457: From our results, due to our experimental conditions and the associated error in our dataset, it is not possible and not our intention to argue in favor of one of these calibrations; This however shows how crucial it is to improve knowledge on the equilibrium $1000\ln\alpha_{carbonate\text{-}water}$ at both high and low temperatures in order to improve the accuracy and precision of our new proxy for reconstructing the $\delta^{18}O_{water}$ from which carbonates, even disequilibrium ones, precipitated.

-Additionnally, the Δ47 based temperature errors are now plotted on the mentioned figure

- ***Section 2.1: I'd like to see some statement about the mineralogy of the carbonates. It looks like that is reported to some extent in the supplement, but I think a sentence on mineralogy of your precipitates should go in the methods.***

We have added a new figure 1 (formerly in the supplementary material) presenting a scanning electron microscopy (SEM) picture of the carbonates and the following lines in section 2.1:

Line 100: The major part of the carbonates precipitated in this study was composed of calcite (Thaler et al., 2017) with minor amounts of aragonite (1 to 4%), vaterite (2 to 4%) and magnesian calcite with low Mg content $(Mg_{0.064},Ca_{0.936})CO_3$ (up to 8%) (Thaler et al., 2017).

- ***Section 3.1 Lines 171 and 172: Maybe mention in the text the equilibrium value and measured value, so that readers do not think -0.27 per mill is the measured value?***

We modified the text as follows:

Line 206: The Δ_{47} offset to equilibrium starts down to -0.270‰ (the largest Δ_{47} offset ever measured in solid carbonates) and the offset to equilibrium reaches -24.7‰ for $\delta^{18}O_{carbonate}$.

- ***Section 3.2 Line 197: Do you know the isotopic composition of the urea? This should be easily testable. I realize it doesn't impact the results of this study, but would be nice to know!***

This is an interesting question to which we had to answer in Thaler et al., 2017. In this study, we measured the $\delta^{13}C$ value of urea, but we still do not know neither its $\delta^{18}O$ value nor its clumped isotope ratio. But even if we could have measured them, the system stays under constrained for the following reasons:

- If urea conversion into dissolved inorganic carbon (DIC) is total, its $\delta^{13}C$ is transferred as is to the DIC (despite the ~12 permil enzymatic fractionation associated with that conversion step), and then to the carbonates if all the DIC precipitates. It is not the case for $\delta^{18}O$ and thus for the clumped isotope ratio, due to the ureolysis reaction mechanism, which is a double hydrolysis (please see below).
- 2/3 of the oxygen atoms in the DIC produced by ureolysis come from water (with an unknown fractionation), and 1/3 from urea (with a fractionation that can be considered = 1 if all of the urea converts into DIC). Thus what matters the most is not the initial isotopic composition of urea but rather the isotopic value of the enzymatic reaction product. In our case, this product can be CO_2 which is then hydrated and/or hydroxylated, a step that adds an additional fractionation step. We unfortunately cannot measure the $\delta^{18}O$ nor the clumped composition of the CO_2 that just got produced.

We however have calculated in Thaler et al.,2017 that:

"With equilibrium initial conditions [we hypothesized here that CO_2 is beeing produced with an isotopic composition in equilibrium with water], CO2(aq) hydration and hydroxylation can explain a 13‰ offset from equilibrium for the $1000\ln\alpha HCO_3^{-}\text{-}H_2O$ value whereas the initial offset from equilibrium observed in solid carbonates was -24.7‰ in the experiment with CA. This demonstrates that CO2 cannot be in oxygen isotope equilibrium with water when it is generated by ureolysis."

Note that in response to one of Pr Bernasconi's comment, we now describe in the manuscript the ureolysis mechanism:

line 82: Ureolysis consists in 2 successive hydrolysis steps: (i) the hydrolysis of urea into ammonia (NH_3) and carbamate ($H_2N\text{-}COOH$) ($H_2N - CO - NH_2 + H_2O \rightarrow NH_3 + H_2N - COOH$), which is catalyzed by urease and is the rate limiting step, and (ii) the rapid and spontaneous hydrolysis of carbamate into ammonia and $CO_{2(aq)}$ ($H_2N - COOH + H_2O \rightarrow NH_3 + CO_{2(aq)} + H_2O$) (Krebs and Roughton, 1948; Matsuzaki et al., 2013) or H_2CO_3 ($H_2N - COOH + H_2O \rightarrow NH_3 + H_2CO_3$) (Mobley and Hausinger, 1989; Krajewska, 2009).

- ***Section 3.3 Line 239: "using the calibration..."***

Correction made

- ***Section 3.4 Lines 278-280: This is true, with the important exception of carbonates in which d13C is also out of equilibrium, which is discussed later in section 3.4.***

That is very true and needed to be highlighted in that sentence. We modified it as follows:

Line 309: "Note that such precision in $\delta^{18}O_{water}$ values found in disequilibrium carbonates is remarkable considering that even for carbonates at isotopic equilibrium for both $\delta^{13}C$ and $\delta^{18}O$, $\delta^{18}O_{water}$ can only be retrieved from paired Δ_{47} and $\delta^{18}O_{carbonate}$ values with a precision of ±1‰ at best (see Supplementary information)."

- ***Line 297: "be explained solely by temperature..."***

Correction made

- ***Line 340: "form in caves from CO2..."***

Correction made

- ***Figure 1: I'm confused by the x-axis. Why is CaCO3 being presented in units of millimolar, which is appropriate for a dissolved solution? A solid should be presented in units of mass, i.e. milligrams, or alternatively as moles precipitated. Figure 2: Same comment as per figure 1.***

This mM unit was chosen to allow comparison with the experiment presented in Thaler et al., 2017. Having the amount of carbonates in mM unit also permits to directly compare it to the amount of DIC and dissolved inorganic nitrogen (DIN) produced in the solution. This latter points out that not all of the DIC precipitates, which has implication for the expression of several fractionation factors.

The comparison between the amount of carbonate formed and the DIN is now available in the new Figure 1, that was previously in the supplementary material of the manuscript

Although we agree mM is an odd unit to use for solids, we see some interest in keeping it that way, and would prefer not to change it.

- ***Figure 5: The trendline symbols for Watkins (2013) and Kim and O'Neil (1997) are too similar, and difficult to distinguish.***

We modified the trendline used.

- ***Also I'm a bit confused by the Watkins data, why are the symbols for Watkins on the same line as Kim and O'Neil yet the trendline lies above?***

We agree this may be confusing, but that is what Watkins et al., 2013 and then Watkins and Hunt 2015 propose.

Below is displayed Figure 5 from Watkins et al., 2013 and its legend, where their data are represented along with cave samples from Coplen, 2007.

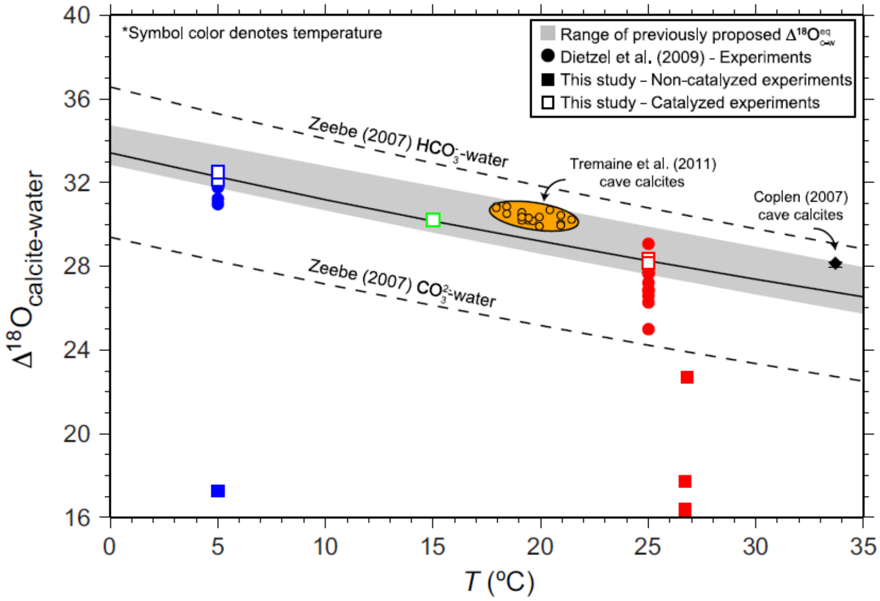


Fig. 5. Relationship between the observed oxygen isotope composition of calcite and temperature. The grey shaded area represents the range of proposed equilibrium values. The dashed lines show the equilibrium oxygen isotope composition of HCO_3^- and CO_3^{2-} relative to water. The solid line is parallel to the equilibrium CO_3^{2-}—water line to illustrate that nearly all of the temperature-dependence of oxygen isotope fractionation between calcite and water can be attributed to the temperature dependence of oxygen isotope fractionation between CO_3^{2-} (or HCO_3^-) and water. The temperature-dependence observed in the literature and in our catalyzed experiments does not necessarily imply oxygen isotope equilibrium between calcite and water. The data point from a natural cave calcite may represent thermodynamic equilibrium; it precipitated several orders of magnitude more slowly than experimental calcites (see Fig. 6).

The experiment catalyzed with CA presented in Watkins et al., 2013 falls on the solid line in their Figure 5. Even though it is not mentioned in the legend, it appears that this solid line is quite hard to distinguish from the line corresponding to Kim and O'Neil (1997) equation (i.e., 1000lna=18.03*1000/(T°C+273.15)-32.42).

As an illustration, at 0°C (where all curves intercept the Y-axis) the $1000\ln\alpha_{calcite\text{-}water}$ value calculated with Kim and O'Neil (1997) equation (in other words $\Delta^{18}O_{calcite\text{-}water}$) equals 33.6, and at 35°C, $1000\ln\alpha_{calcite\text{-}water}$ equals 26.1.

Accordingly, Watkins et al., 2013's catalyzed experiment is indeed on the same trendline as Kim and O'Neil, 1997, below the cave carbonates of Coplen, 2007.

However, we have also reproduced, again below, Figure 6 from Watkins et al., 2013 with its legend, where the model calibration equation ($\Delta^{18}Oeq_{calcite\text{-}water}$=17747/(T°C+273,15)-29.777) is given:

At 0°C, $\Delta^{18}Oeq_{calcite\text{-}water}$ = 35.2 and at 35°C, $\Delta^{18}Oeq_{calcite\text{-}water}$ = 27.8 (On Watkins et al., 2013's Figure 5, these two points are above the solid line).

So indeed, Watkins et al., 2013's model follows Coplen (2007) trendline even though the CA-catalyzed experiment datapoints fall on Kim and O'Neil (1997) curve. The catalyzed experiment datapoints fall on Watkins et al (2013) model trend line when represented against the precipitation rate (logR) that is incorporated in the calculation that produced Figure 6 lines. However, no 1000lnα equation corrected for logR value is given in the figure.

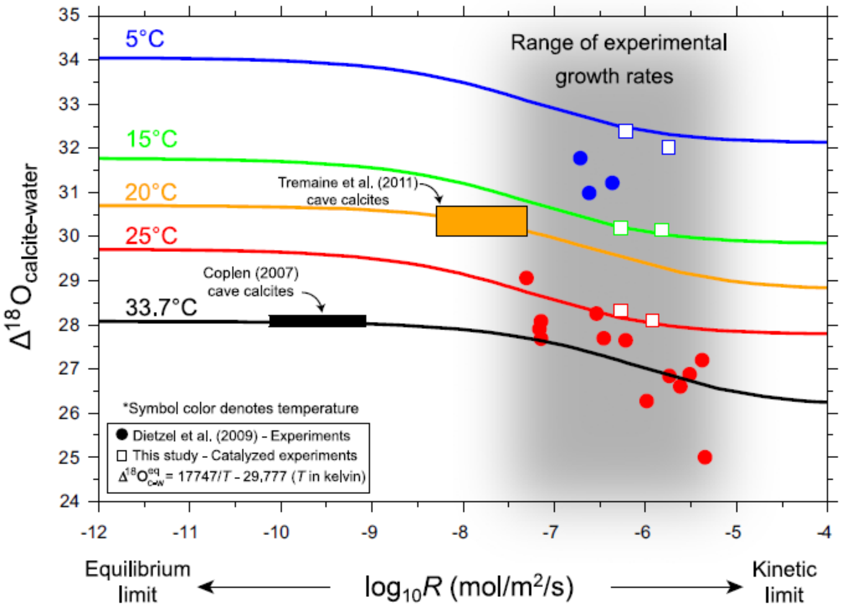


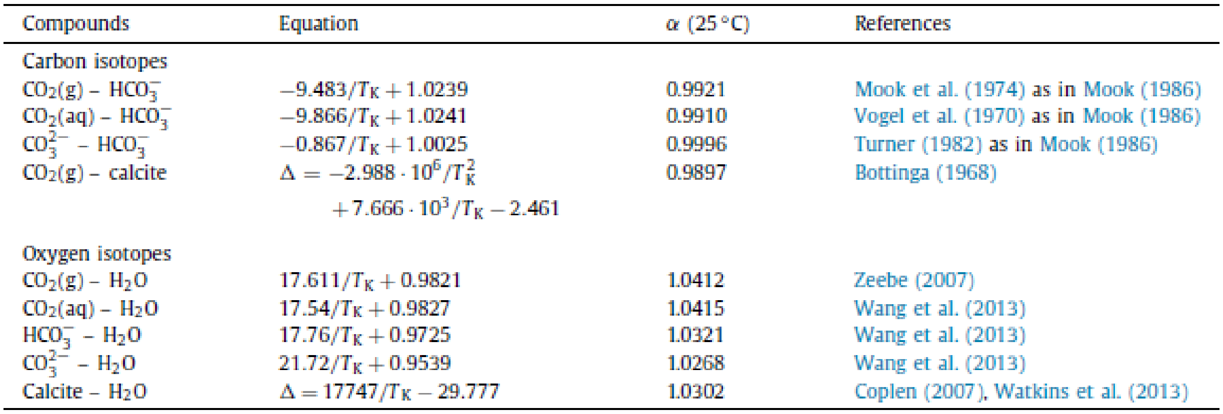
Fig. 6. $\Delta^{18}O_{c\text{-}w}$ versus precipitation rate R. The model curves describe the rate-dependence on $\Delta^{18}O_{c\text{-}w}$ while accommodating the equilibrium $\Delta^{18}O_{c\text{-}w}$ at 33.7 °C and $pH = 7.4$ inferred from natural cave calcite (Coplen, 2007). The slowly grown cave calcites from Tremaine et al. (2011) formed at about 20 °C and $pH = 7.8$. In the model, the temperature dependence arises solely from temperature-dependent partitioning of oxygen isotopes between DIC species and water. The pH dependence arises from the difference in HCO_3^- versus CO_3^{2-} participating in calcite growth as a function of growth rate. The data of Dietzel et al. (2009) are isotopically light, which may be a consequence of isotopic disequilibrium among DIC species in the bulk solution from which calcite is precipitated. Such a disequilibrium effect is not incorporated into the model. An important insight from the agreement between model and data is that direct measurement of equilibrium $\Delta^{18}O_{c\text{-}w}$ by conventional methods may require experiments that last years to decades.

As you might wonder, Coplen (2007) exact equation is:

$$\boxed{1000 \ln \alpha_{\text{calcite–water}} = 17.4(1000/T) - 28.6 \qquad (3)}$$

To confirm previous statements (that is a bit puzzling), below is Table 1 from Watkins and Hunt, 2015 with the calcite-water equilibrium equation used. Again Coplen, 2007 and Watkins et al., 2013 are undistinguishable:

Table 1
Compilation of equilibrium fractionation factors (α^{eq}_{i-j} unless otherwise noted) for carbon and oxygen isotopes in aqueous solution. These equations are presented graphically in Fig. 1 (note: $\Delta = 1000 \ln \alpha$).



Compounds	Equation	α (25 °C)	References
Carbon isotopes			
$CO_2(g) - HCO_3^-$	$-9.483/T_K + 1.0239$	0.9921	Mook et al. (1974) as in Mook (1986)
$CO_2(aq) - HCO_3^-$	$-9.866/T_K + 1.0241$	0.9910	Vogel et al. (1970) as in Mook (1986)
$CO_3^{2-} - HCO_3^-$	$-0.867/T_K + 1.0025$	0.9996	Turner (1982) as in Mook (1986)
$CO_2(g)$ – calcite	$\Delta = -2.988 \cdot 10^6/T_K^2 + 7.666 \cdot 10^3/T_K - 2.461$	0.9897	Bottinga (1968)
Oxygen isotopes			
$CO_2(g) - H_2O$	$17.611/T_K + 0.9821$	1.0412	Zeebe (2007)
$CO_2(aq) - H_2O$	$17.54/T_K + 0.9827$	1.0415	Wang et al. (2013)
$HCO_3^- - H_2O$	$17.76/T_K + 0.9725$	1.0321	Wang et al. (2013)
$CO_3^{2-} - H_2O$	$21.72/T_K + 0.9539$	1.0268	Wang et al. (2013)
Calcite – H_2O	$\Delta = 17747/T_K - 29.777$	1.0302	Coplen (2007), Watkins et al. (2013)

- ***Additionally, if it doesn't clutter up the plot too much it would be good to see the error bars on the carbonate datapoints.***

-We chose to only mention the error on our data point in the legend, not only to not clutter up the plot, but also because no error is given in Kim and O'Neil, 1997, which makes error comparison between datasets complicated. We thus chose to not represent any error in the first place. However, please note that the symbol size is quite big and probably encompass the error (if it is of around 0.3 or 0.4 permil, which is plausible).

-The Δ_{47} based temperature errors are now plotted on the mentioned figure. The following sentence has also been added to the associated legend:

"X-axis errors for this study are included in the symbol size. The Y-axis error for all the reconstructed temperature is given in the figure."

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