

LETTER:
COMMENTS ON PROCESSES CONTRIBUTING TO THE ISOTOPE
COMPOSITION OF ^{13}C AND ^{18}O IN CALCITE DEPOSITED TO
SPELEOTHEMS

O PROCESIH, KI VPLIVAJO NA IZOTOPSKO SESTAVO ^{13}C IN ^{18}O
V KALCITNIH SIGAH

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INTRODUCTION

Isotope compositions of carbon and oxygen in calcite deposited to stalagmites are regarded as important proxies for paleo-climate. The number of papers reporting such proxies rises rapidly. Additionally cave monitoring is being performed to observe chemical properties of the water dripping to speleothems, the partial pressure of CO_2 in the soil above the cave and in the cave atmosphere, and other parameters outside the cave to relate recent climate conditions to recently deposited calcite.

There are, however, physical and chemical processes independent of climatic conditions, which also contribute to the isotope composition and which can add noise to the climate signal. In this letter I resume these from the current literature to open a more easy access to this problem than available from the current original publications.

THE CHEMICAL EVOLUTION OF WATER ON ITS WAY FROM ENTERING THE CAVE
TO THE DRIP SITE AND DURING PRECIPITATION OF CALCITE

Water entering the cave mostly is in chemical equilibrium with respect to calcite. Its pH-value depends only on temperature and Ca-equilibrium-concentration as depicted in Fig. 1.

For $[\text{Ca}]_{\text{eq}} = 2 \text{ mmol/L}$, pH is about 7.3. P_{CO_2} in this solution exceeds P_{CO_2} in the cave. Since CO_2 in the solution is present as molecular carbon dioxide degassing occurs by molecular diffusion when the water gets into contact with the cave atmosphere. In most cases each drip site has a catchment area, e.g. a stalactite, from which the water flows in thin films of about 0.01 cm thickness to-

wards the drip site contributing to drip formation. Fig. 2 illustrates the chemical evolution of the water on its way to the drip site.

Degassing of CO_2 from a thin water layer into the cave atmosphere is fast, with an exponential approach with time constant $\tau_{\text{deg}} = 4\delta^2/(\pi^2 D_m)$. δ is film thickness and D_m is the coefficient of molecular diffusion ($1 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). At 10° C $\tau_{\text{deg}} = 3.5 \text{ s}$ for $\delta = 0.01 \text{ cm}$. To achieve 95% of equilibrium the time $T_{\text{deg}} = 3 \cdot \tau_{\text{deg}}$ is needed. (Buhmann & Dreybrodt 1985, Dreybrodt 1988)

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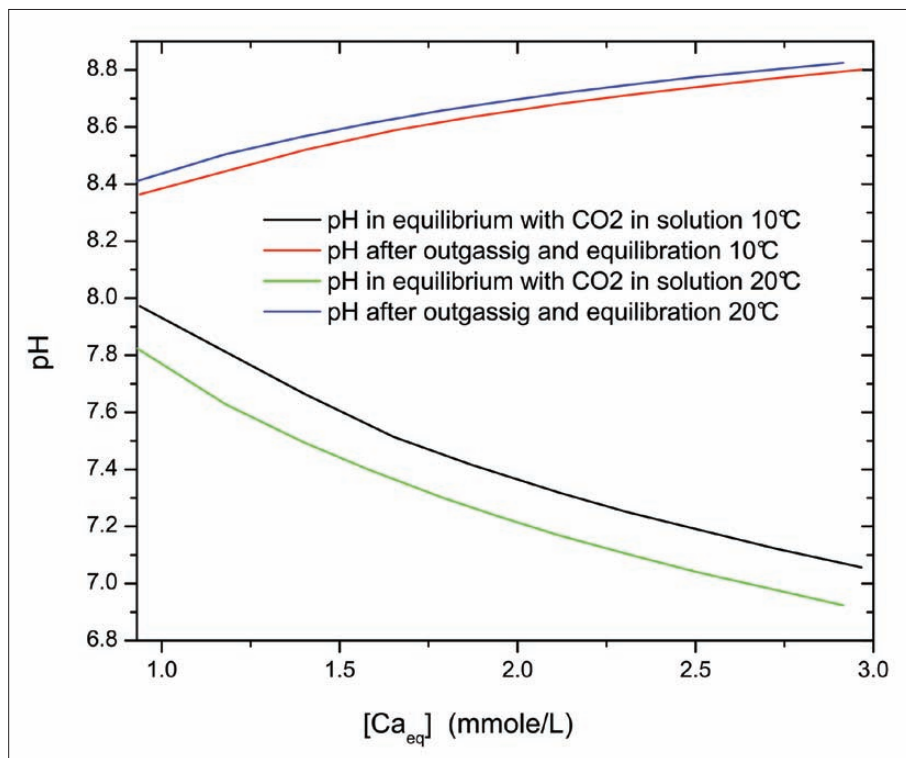


Fig. 1: Water entering the cave is in chemical equilibrium with respect to calcite. The corresponding pH-values are given as a function of the calcium- equilibrium- concentration for 10°C and 20°C. After degassing and equilibration of the carbonate system with respect to the $P_{CO_2} = 0.0004 \text{ atm}$ in the cave atmosphere pH rises to values above 8. Calculated by use of PHREEQC version 2 (Parkhurst & Appelo 1999).

After out gassing is completed (red line in Figure 2) pH, $[HCO_3^-]$, and $[CO_3^{2-}]$ are no longer in equilibrium with respect to the lower concentration of CO_2 in the solution. Establishing chemical and isotopic equilibrium (blue line) needs the time $T_{eq} = 3 \cdot \tau_{eq} = 321 \text{ s}$. (Dreybrodt & Scholz 2011; Zeebe *et al.* 1999) and causes an increase in pH and supersaturation with respect to calcite. The pH-values after completion of this process, higher by about one pH-unit are shown also in Fig. 1. Since the time T_{eq} of equilibration is one order of mag-

nitude higher than the time T_{deg} of degassing both Ca-concentration and pH stay almost constant during degassing.

By measuring pH at the drip site with a micro- pH-electrode, which needs only one drop of solution, one is able to find out if degassing is already completed. For values of about 7.5 one can assume that one still deals with a solution saturated with respect to calcite, whereas pH-values above 8.3 indicate degassing and equilibration with respect to the P_{CO_2} in the cave atmosphere.

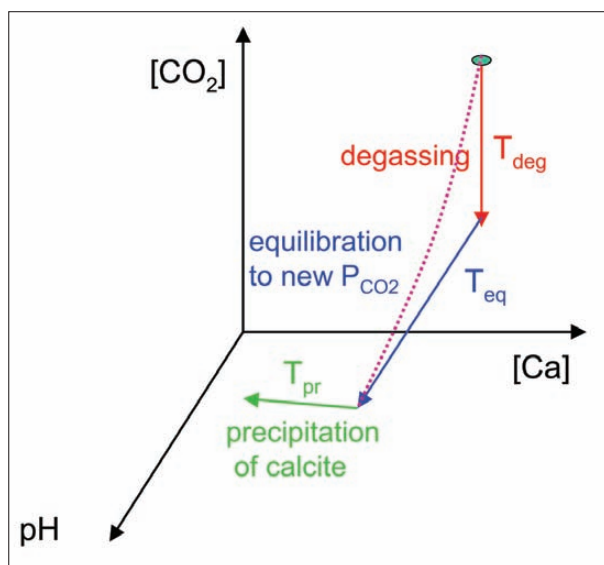


Fig. 2: Reaction pathways and the time needed to achieve equilibrium for each of them. In step 1 (degassing) pH and [Ca]-concentration stay constant. In step 2 (equilibration to new P_{CO_2}) pH increases, but Ca-concentration remains almost unaltered. During precipitation (step3) pH decreases slightly with decreasing calcium concentration. The dotted line schematically depicts the chemical pathway when the time of degassing is on the same order of magnitude as the time needed for equilibration.

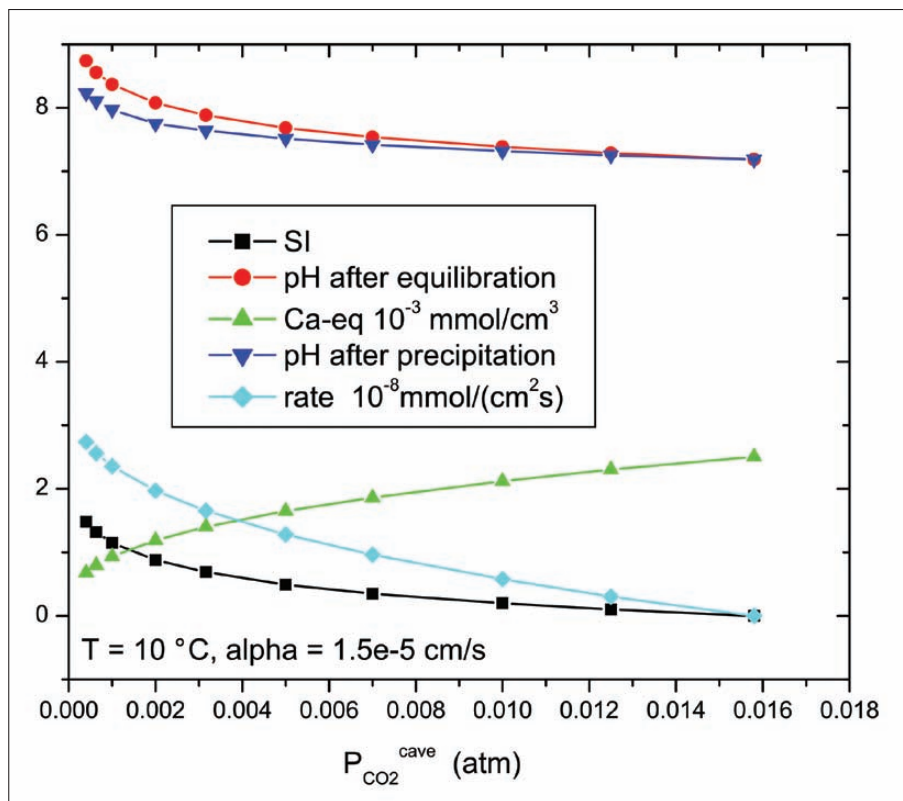


Fig. 3: Chemical equilibrium concentrations Ca-eq , pH , and saturation index SI after out gassing into a cave with $P_{\text{CO}_2}^{\text{cave}}$ and subsequent equilibration. The initial precipitation rates $R = \alpha \cdot (C_{\text{in}} - C_{\text{eq}})$ at the onset of precipitation and the pH -values after completion of precipitation are also shown. $\alpha = 1.5 \cdot 10^{-5}\text{ cm s}^{-1}$. The values of Ca-eq are the calcite concentrations in equilibrium with $P_{\text{CO}_2}^{\text{cave}}$. Note that the rates decline with increasing $P_{\text{CO}_2}^{\text{cave}}$. Calculated by use of PHREEQC version 2 (Parkhurst & Appelo 1999).

After equilibrium and correspondingly supersaturation are attained calcite begins to precipitate (green line in fig. 2). Precipitation rates (blue line in Fig. 3) are given by $R = \alpha \cdot (C - C_{\text{eq}})$. α is a temperature dependent rate constant, C is the actual calcium-concentration, and C_{eq} is the calcium concentration in equilibrium with the P_{CO_2} in the solution. During precipitation C_{eq} is approached exponentially with time constant $\tau_{\text{prec}} = \delta/\alpha$. At 10°C $\tau_{\text{prec}} = 780\text{ s}$ and $T_{\text{prec}} = 3 \cdot \tau_{\text{prec}} = 2340\text{ s}$ is much larger than T_{eq} (Buhmann & Dreybrodt 1985; Dreybrodt 1988; Baker *et al.* 1998). During precipitation the Ca -concentration decreases and pH becomes lower by less than 0.5 pH -units (Dreybrodt & Scholz 2011).

For each CaCO_3 unit attached to the calcite surface one molecule of CO_2 is released by the reaction $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$ and degasses by molecular diffusion. This out gassing is driven by precipitation of calcite and must not be confused with degassing in step 1.

Fig. 3 illustrates pH after degassing and equilibration as a function of the P_{CO_2} in the cave atmosphere. Also are given the precipitation rates, the value of C_{eq} (Ca-eq), in equilibrium with the cave atmosphere and the saturation index SI . Note that this figure shows these values after equilibration at the onset of precipitation. The pH -value after completion of precipitation is also shown.

Summarizing: Three steps determine the precipitation of calcite:

1) Physical out gassing in time scales of 10s for water films with thickness $\delta < 0.02\text{ cm}$.

2) Subsequent equilibration of pH , $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ and establishment of supersaturation in time scales of 100s.

3) Precipitation of calcite in time scales of 1000s.

Since these time scales are all different by one order of magnitude in a first approximation these 3 steps can be regarded as subsequent in time and Fig. 1 is an appropriate representation of reality.

One comment must be given here. If the time of out gassing due to larger film thickness δ is on the same order of magnitude as the equilibration time these two steps occur simultaneously as depicted schematically by the dotted curve in Fig. 1. If the time to attain equilibrium is still one order of magnitude smaller than the time needed for precipitation this has no consequences for the following arguments.

If the water dripping to a stalagmite has not achieved full equilibration when it impinges to the stalagmite the saturation index SI has not reached its maximal value and consequently deposition rates also stay low. This applies for travel times $T < T_{\text{eq}}$. In this case calcite deposition will not start at the impact point of the drip but at some distance away from it, which the water has reached after the time T_{eq} . This might explain, why many drip sites do not show stalagmites below.

ISOTOPIC EVOLUTION OF THE CARBONATE SPECIES IN THE WATER ON ITS WAY DOWN TO THE CAVE

Rainwater seeping through the soil takes up CO_2 and subsequently dissolves CaCO_3 from the rock. The isotope compositions of both carbon and oxygen in the soil- CO_2 are different from that in the limestone. Therefore after completion of dissolution both the isotope compositions of the rock and that of the soil- CO_2 determine the isotope compositions of carbon and oxygen in the water. For carbon the carbonate system is closed and all carbon atoms are contained in it. The isotope composition remains fixed once dissolution is completed and neither degassing or calcite precipitation has yet occurred.

This is not the case for the oxygen atoms in the carbonate species because they can be exchanged with those in the water molecules by the reactions $\text{CO}_2 + \text{H}_2^{18}\text{O} \rightleftharpoons \text{H}^+ + \text{HC}^{18}\text{OO}_2^-$ and $\text{CO}_2 + {}^{18}\text{OH}^- \rightleftharpoons \text{HC}^{18}\text{OO}_2^-$, which can be summarized as exchange reaction $\text{HCO}_3^- + \text{H}_2^{18}\text{O}$

$\rightleftharpoons \text{HC}^{18}\text{OO}_2^- + \text{H}_2\text{O}$. The number of oxygen atoms in the water molecules exceeds that of the oxygen atoms contained in the carbonate species by a factor of 10^4 . Therefore finally after sufficiently long time the oxygen atoms in the carbonate will be in isotopic equilibrium with those in the water, representing the isotope composition of the rainwater as climatic signal. At 20°C the exchange time for isotopic equilibrium with the oxygen in the water is $T_{\text{ex}} = 3 \cdot \tau_{\text{ex}} = 30.000\text{s}$. Consequently at least 8 hours are needed until 95% of isotopic equilibrium is reached, at 10°C this time increases to 29 hours and at 5°C to 54 hours (Beck 2004; Beck *et al.* 2005). Therefore the travel time of the water from the surface to the cave must be at least T_{ex} . Otherwise the isotope composition of the oxygen in the carbonate species in the water entering the cave does not represent a climatic signal.

INFLUENCE OF THE EXCHANGE REACTION TO THE ISOTOPE COMPOSITION OF OXYGEN IN THE CARBONATE

In addition, as a consequence of these long exchange times, at least one order of magnitude larger than the time for precipitation, buffering with the huge oxygen reservoir in the water during precipitation of calcite does not change the isotopic composition of oxygen in the carbonate. Furthermore, evaporation of water from the water film changes the isotope composition of oxygen in the water by Rayleigh distillation, but it will not affect the isotopic composition of oxygen in the carbonate. In other words, the oxygen reservoir in the carbonate species cannot react with the oxygen in water because the exchange time is about thirty times longer than the precipitation time.

If the water precipitates calcite during drip times $T_d \leq 0.1 \cdot \tau_{\text{prec}}$ deposition rates at the apex are practically constant in time. The isotopic composition of the drip water carbonate both with respect to carbon and oxygen increases due to kinetic Rayleigh distillation by less than 0.3‰ (Dreybrodt & Scholz, 2011). For drip times $T_d > 3 \cdot \tau_{\text{prec}}$ both ^{13}C and ^{18}O can become more heavy by a few per mille due to Rayleigh-distillation (Dreybrodt 2008; Scholz *et al.* 2009; Dreybrodt and Scholz 2011).

If the water needs a time much longer than T_{eq} to reach the drip site, prior calcite precipitation (PCP) at the cave walls can occur as seen from many calcite crusts in the vicinity of drip sites. This can cause drastic enrichment in both ^{13}C and ^{18}O in the calcite precipitated at the apex of the stalagmite (Dreybrodt & Scholz 2011). Recently Sherwin and Baldini (2011) observed PCP on stalactites and on cave ceilings.

Flow velocities along the walls of a cave or down a stalactite are on the order of 0.1 cm/s . Therefore water from sources, e.g. a joint, about half a meter away from the dripping site are ideal candidates for delivering drip water in chemical and isotopic equilibrium needed to record climate conditions at the surface above the cave.

The catchment area and flow velocities can be determined by putting a tiny drop of uranine above the dripping site. Shining UV-light to it marks the pathway of the water from that point and the time until it reaches the drip site can be determined. We have done such experiments successfully. Fig. 4 shows an illustration.

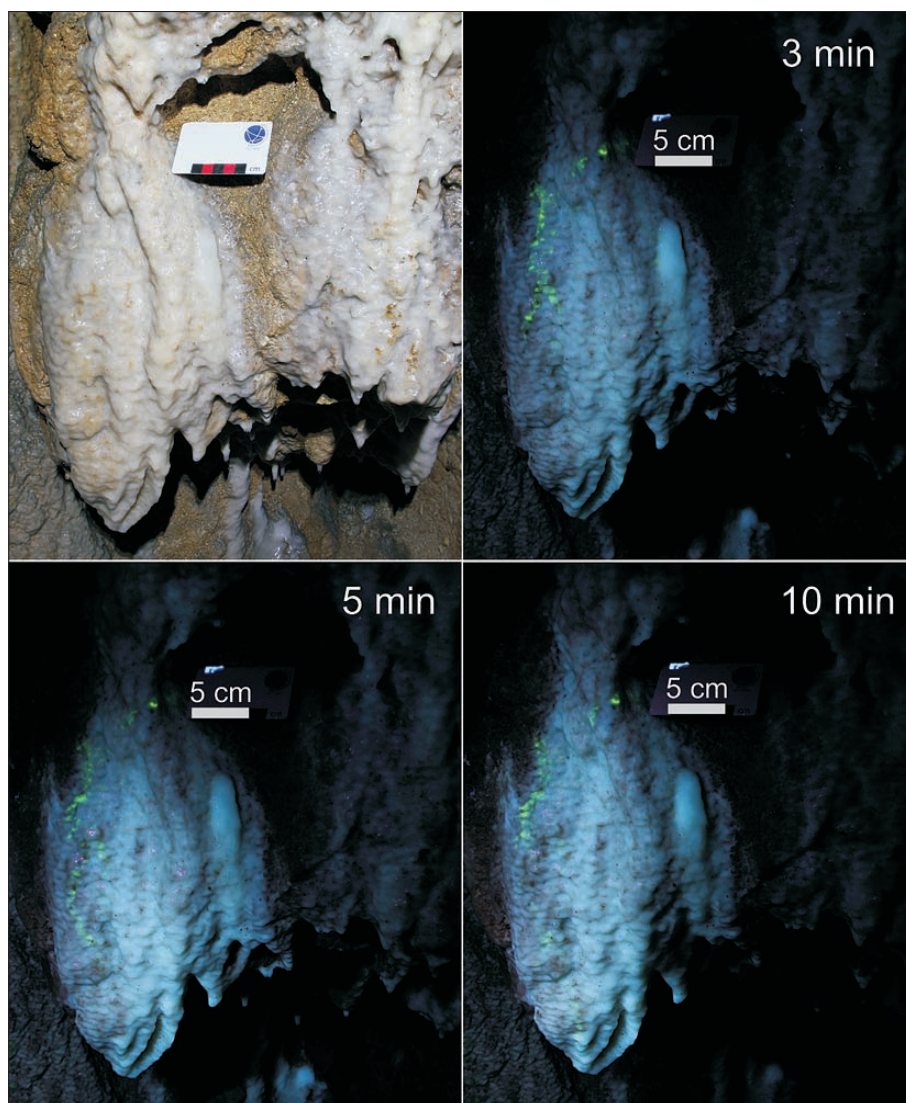


Fig. 4: Flow of water film towards the tip of stalagmite. The water was dyed by fluorescent tracer. The situation at different times as denoted on the pictures was photographed with UV illumination. (Photo: F. Gabrovšek)

REFERENCES

- Baker, A., Genty, D., Dreybrodt, W., Barnes, W.L., Mockler, N.J. & J. Grapes, 1998: Testing theoretically predicted stalagmite growth rate with recent annually laminated samples implications for past stalagmite deposition.- *Geochim. Cosmochim. Acta*, 62, 393–404.
- Beck, W.C., Grossman, E.L. & J.W. Morse, 2005: Experimental studies of oxygen isotope fractionation in the carbonic acid system at 15°, 25°, and 40°C.- *Geochim. Cosmochim. Acta*, 69, 3493–3503.
- Buhmann, D. & W. Dreybrodt, 1985: The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas: 1. Open system.- *Chem. Geol*, 48, 189–211.
- Dreybrodt W., 1988: *Processes in Karst Systems - Physics, Chemistry, and Geology*.- Springer, pp. 288, Berlin.
- Dreybrodt, W., 2008: Evolution of the isotopic composition of carbon and oxygen in a calcite precipitating $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ solution and the related isotopic composition of calcite in stalagmites.- *Geochim. Cosmochim. Acta*, 72, 4712–4724.

- Dreybrodt, W. & D. Scholz, 2011: Climatic dependence of stable carbon and oxygen isotope signals recorded in speleothems: From soil water to speleothem calcite.- *Geochim. Cosmochim. Acta*, 75, 734–752.
- Parkhurst D. L. & C.A.J. Appelo, 1999: User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations.- U.S. Geological Survey Water-Resources Investigations Report 99–4259, pp. 312, Denver, Colorado.
- Sherwin, C.M. & J.U.L. Baldini, 2011: Cave air and hydrological controls on prior calcite precipitation and stalagmite growth rates: implications for palaeoclimate reconstructions using speleothems, *Geochimica et Cosmochimica Acta*, 75, 3915–3929.
- Scholz D., Mühlinghaus C. & A. Mangini, 2009: Modelling $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the solution layer on stalagmite surfaces.- *Geochim. Cosmochim. Acta*, 73, 2592–2602.
- Zeebe R. E., Wolf-Gladrow D. A. & H. Jansen, 1999: On the time required to establish chemical and isotopic equilibrium in the carbon dioxide system in seawater. -*Marine Chemistry*, 65, 135–153.