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 [Ca]$_{eq}$ = 2 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 towards 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 $\tau_{deg} = 4\delta^2/(\pi^2D_m)$. $\delta$ is film thickness and $D_m$ is the coefficient of molecular diffusion ($1 \cdot 10^{-5}$ cm$^2$ s$^{-1}$). At 10°C $\tau_{deg} = 3.5$ s for $\delta = 0.01$ cm. To achieve 95% of equilibrium the time $T_{deg} = 3 \cdot \tau_{deg}$ is needed. (Buhmann & Dreybrodt 1985, Dreybrodt 1988)

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After out gassing is completed (red line in Figure 2) pH, $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ 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 $T_{eq} = 3 \cdot \tau_{eq} = 321$ 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 magnitude 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 $P_{\text{CO}_2}$ in the cave atmosphere.

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 $P_{\text{CO}_2} = 0.0004$ atm in the cave atmosphere pH rises to values above 8. Calculated by use of PHREEQC version 2 (Parkhurst & Appelo 1999).

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 $P_{\text{CO}_2}$) pH increases, but Ca-concentration remains almost unaltered. During precipitation (step 3) 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.
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 \( R = \alpha \cdot (C - C_{eq}) \). \( \alpha \) 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 \( \tau_{\text{prec}} \approx 780 \text{ s} \) and \( T_{\text{prec}} \approx 3 \cdot \tau_{\text{prec}} \approx 2340 \text{ s} \) is much larger than \( T_{\text{eq}} \) (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 HCO\(_3\)\(^-\) + H\(^+\) → H\(_2\)O + 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, [HCO\(_3\)\(^-\)], and [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 \( \delta \) 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 \( T_{\text{eq}} \). 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 CO₂ and subsequently dissolves CaCO₃ from the rock. The isotope compositions of both carbon and oxygen in the soil-CO₂ are different from that in the limestone. Therefore after completion of dissolution both the isotope compositions of the rock and that of the soil-CO₂ 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 CO₂ + H²¹⁸O ⇌ H⁺ + HCO¹⁸O⁻ and CO₂ + ¹⁸OH⁻ ⇌ H¹⁸CO₂⁻, which can be summarized as exchange reaction HCO₃⁻ + H₂¹⁸O ⇌ HC¹⁸OO₂⁻ + H₂O. The number of oxygen atoms in the water molecules exceeds that of the oxygen atoms contained in the carbonate species by a factor of 10⁴. Therefore 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 $T_{ex} = 3 \cdot \tau_{ex} = 30.000s$. 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 $T_{eq}$. 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 $T_d \leq 0.1 \cdot \tau_{prec}$ 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%/o (Dreybrodt & Scholz, 2011). For drip times $T_d > 3 \cdot \tau_{prec}$ both ¹³C and ¹⁸O 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 ¹³C and ¹⁸O 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.
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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


