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Modelling the $\delta^{18}O$ value of cave drip water and speleothem calcite

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ABSTRACT

Stable isotope signals recorded in speleothems have provided important insights about past climate variability in recent years. Quantitative reconstruction of mean annual temperature and the amount of precipitation, however, remains difficult because the stable isotope signals are influenced by various processes.
Here we present a drip water model, which shows how these climate parameters affect the oxygen isotope signal of cave drip water. In the model the dependence of the $\delta^{18}O$ value of drip water on mean annual temperature is established by correlation to the amount of winter precipitation and winter temperature. Application of the model to two caves in western Germany reveals a strong influence of winter rainfall on the oxygen isotope composition of cave drip water in this region. Assuming equilibrium isotope fractionation between drip water and calcite, we provide a function relating the $\delta^{18}O$ value of speleothem calcite to mean annual surface temperature. This function shows a clear anticorrelation between temperature and the $\delta^{18}O$ value of speleothem calcite, which has been previously reported for several caves in central and northern Europe. By inverse application of this function, we tentatively reconstruct average temperatures for the period between 6 and 1.5 ka from the $\delta^{18}O$ signals of two stalagmites from Atta and Bunker Cave (western Germany). The resulting temperature curves are very sensitive to the value used for the correlation between the amount of winter precipitation and winter temperature. Since this correlation was probably not constant in the past, the reconstructed temperature curves are associated with substantial uncertainty.

1. Introduction

Speleothems are a valuable archive of past climate variability since they (i) grow continuously over thousands of years in sheltered cave environments, (ii) allow precise dating using the Th/U-method (Richards and Dorale, 2003; Scholz and Hoffmann, 2008) and (iii) offer several proxies that can be measured at high-resolution. Stalagmites record the climatic conditions above the cave in their stable carbon and oxygen isotope signals ($\delta^{13}C$ and $\delta^{18}O$) and also in various trace elements such as magnesium or strontium (Fairchild and Treble, 2009).

In this study we focus on the oxygen isotope signal recorded in stalagmites and introduce a drip water model developed in order to better understand the influence of different climate parameters on the $\delta^{18}O$ value of cave drip water and, in particular, the influence of temperature variability. The model is based on general processes influencing the $\delta^{18}O$ signal of cave drip water and can, thus, be applied to any cave system worldwide.

The $\delta^{18}O$ signal of speleothem calcite is affected by (i) the $\delta^{18}O$ value of the drip water feeding the stalagmite and (ii) isotope fractionation processes occurring during calcite precipitation. The latter have been discussed and modelled in several studies (Dreybrodt, 2008; Hays and Grossman, 1991; Kim and O'Neil, 1997; Mühlinghaus et al., 2009; O'Neil et al., 1969; Scholz et al., 2009). In case of equilibrium isotope fractionation the relation between the $\delta^{18}O$ of the precipitated calcite and cave temperature is about −0.23‰/°C (Friedman and O'Neil, 1977; Kim and O'Neil, 1997; O'Neil et al., 1969). Recent results, however, indicate that most speleothem $\delta^{18}O$ records may be influenced by disequilibrium isotope fractionation (Mickler et al., 2006). In this case the $\delta^{18}O$ signal also depends on other parameters, such as the drip rate feeding the stalagmite and supersaturation with respect to calcite. The effect of disequilibrium isotope fractionation is particularly enhanced for slow drip rates and/or high supersaturation with respect to calcite (Mühlinghaus et al., 2009). These processes may, thus, attenuate oramplify the temperature dependence of the $\delta^{18}O$ signal. Quantitative modelling of disequilibrium isotope fractionation processes in speleothems has been increasingly performed in recent years (Mühlinghaus et al., 2009; Romanov et al., 2008; Scholz et al., 2009). The absolute values resulting from these models, however, are related with some uncertainty due to the uncertainty in the corresponding fractionation factors and chemical constants. In general, the relationship of lower $\delta^{18}O$ values for increasing temperature, as expected for equilibrium isotope fractionation, is maintained (Mühlinghaus et al., 2009).

An ideal model of speleothem $\delta^{18}O$ signals in dependence of climatic parameters such as temperature and precipitation would combine a drip water model with a model describing the isotope

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fractionation processes. Due to the above mentioned uncertainties of the latter we focus on the processes affecting the $\delta^{18}O$ value of the drip water here. The absolute values resulting from our model, especially when the model is inversely applied in order to reconstruct past temperature, may, therefore, be associated with some uncertainty. The general relationships, however, are reliable.

The $\delta^{18}O$ signal of cave drip water is affected by various processes: (i) Processes affecting the $\delta^{18}O$ value of meteoric precipitation such as the altitude effect, the amount effect, the continental effect, temperature and the source of the water vapour. These processes have been described in detail for instance in Mook (2006) and the review papers of McDermott (2004) and Lachniet (2009). (ii) Processes occurring in the soil and karst above the cave, such as averaging meteoric water of several months, calcite dissolution and the recycling of seepage water by evapotranspiration. These processes strongly depend on the type of vegetation above the cave and the constitution of the soil (Lachniet, 2009). (iii) Seasonality of meteoric precipitation. This results in the $\delta^{18}O$ values of the drip water to be biased towards the $\delta^{18}O$ signal of the season with the highest contribution to the annual amount of meteoric precipitation (Cruz et al., 2005a; Johnson et al., 2006; Van Beynen and Febbroriello, 2006).

It has been shown for many caves worldwide that the $\delta^{18}O$ value of both drip water and speleothem calcite reflects the surface climate of the cave environment (e.g., Cheng et al., 2009; Cruz et al., 2005b; Fleitmann et al., 2003a,b; Mangini et al., 2005; McDermott et al., 2001; Partin et al., 2007; van Breukelen et al., 2008; Wang et al., 2001). This might be due to changes in different climatic parameters such as changes in synoptic patterns, which affect the air mass trajectories, the source and amount of precipitation and surface temperature.

Temperature reconstructions using speleothem $\delta^{18}O$ signals, however, remain difficult. McDermott et al. (2001) found a positive correlation between the $\delta^{18}O$ value of speleothem calcite and temperature for a stalagmite from Crag Cave, Ireland. In other caves, however, a negative relationship has been observed (Genty et al., 2006; Lauritzen and Lundberg, 1999; Mangini et al., 2005; Sundqvist et al., 2010). This shows that the response of different regions and caves to surface climate warming may be opposite and highlights the complexity of the system.

For caves in northern and central Europe a negative relationship between temperature and speleothem $\delta^{18}O$ is particularly surprising. In these latitudes temperature is the major control of the $\delta^{18}O$ value of meteoric precipitation, and the observed spatial relationship between temperature and the $\delta^{18}O$ value of meteoric precipitation ranges from $+0.17$ to $+0.9$‰/°C (Dansgaard, 1964; Mook, 2006; Rozanski et al., 1993; Schmidt et al., 2007). The values expected for the temporal temperature gradient should be smaller but still positive (Fricke and O'Neil, 1999). Schmidt et al. (2007) determine the temporal temperature gradient to be 0.3‰/°C for central and northern Europe. Consequently, one also expects a positive relationship between the $\delta^{18}O$ value of speleothem calcite and surface temperature. This effect may be compensated by the negative relationship between the $\delta^{18}O$ value of speleothem calcite and temperature resulting from isotope fractionation effects during calcite precipitation and other processes. In total, however, the expected relationship between surface temperature and the $\delta^{18}O$ value of speleothem calcite is positive. In this paper we present an explanation for the negative relationship between temperature and the $\delta^{18}O$ value of speleothem calcite observed for some caves.

2. The drip water model

Cave drip water is a mixture of the meteoric water infiltrating the soil above the cave, and its $\delta^{18}O$ value depends on both climate and vegetation parameters. The drip water model was developed in order to understand how and to what extent these parameters affect the $\delta^{18}O$ value of the drip water. The model describes the evolution of the $\delta^{18}O$ value from meteoric precipitation to cave drip water. Climatic effects influencing the $\delta^{18}O$ value of meteoric precipitation as well as effects in the soil zone (i.e., evaporation, transpiration and enrichment of soil water with CO_2) are included. Other processes, such as prior calcite precipitation or mixing between pore water and ground water, are not taken into account.

The drip water model is based on the assumption that the annual mean $\delta^{18}O$ value of cave drip water is the sum of the weighted monthly mean $\delta^{18}O$ value of meteoric precipitation (Yonge et al., 1985):

$$\delta^{18}O_{\mathrm{annualmean}} = \sum_i G_i(T, P, F, h) \cdot \delta^{18}O_{\mathrm{monthlymean}_i}(T), \quad (1)$$

where G_i is the weighting coefficient for each month, which depends on surface temperature, T, the amount of meteoric precipitation, P, relative humidity, F, and a coefficient describing the type of vegetation, h (see Section 2.1 for details). $\delta^{18}O_{\mathrm{monthlymean}}$ is the monthly mean $\delta^{18}O$ value of the water infiltrating deeper soil layers.

This assumption was shown to be reasonable for caves from Central Europe (McDermott, 2004) and has been validated by several cave monitoring programs (Lauritzen and Lundberg, 1999; Riechelmann, 2010; Riechelmann et al., 2010; Sundqvist et al., 2007).

2.1. The weighting coefficient

The weighting coefficient, G_i, for a particular month is the fraction of the annual amount of water infiltrating into deeper soil layers and subsequently into the cave during this month:

$$G_i = \frac{\mathrm{Inf}_i}{\sum_i \mathrm{Inf}_i} \quad (2)$$

Inf_i is the amount of infiltrating water, i.e., the amount of precipitation falling above the cave minus the water lost due to evapotranspiration, ET.

$$\mathrm{Inf}_i = \mathrm{Precipitation} - \mathrm{ET} \quad (3)$$

Several equations for the estimation of potential evapotranspiration have been developed (Haude, 1954, 1955; Penman, 1948; Thornthwaite and Mather, 1957). Here we use the equation established by Haude (1954, 1955):

$$\mathrm{ET}_{\mathrm{pot}} = h \cdot P_{2p.m.} \cdot (1 - F_{2p.m.}/100) \left[\frac{\mathrm{mm}}{\mathrm{day}}\right], \quad (4)$$

where

$$P_{2p.m.} = 4.58\mathrm{hPa} \cdot 10^{\left(7.45 \cdot T_{2p.m.}/235 + T_{2p.m}\right)} [\mathrm{hPa}]. \quad (5)$$

$P_{2p.m.}$, $F_{2p.m.}$ and $T_{2p.m.}$ are the saturation vapour pressure, relative humidity and temperature at 2 p.m., respectively. The type of vegetation is described by the vegetation coefficient, h (Häckel, 1999).

The equation of Haude (1954, 1955) has three advantages compared to other equations: a) the type of vegetation is included, which is an important parameter because the amount of evapotranspiration is bound to depend on it. Whereas the values for h for uncovered soil and grassland are relatively constant throughout the year, trees reduce the evaporation due to the shielding by their canopy, and their uptake of water follows the annual pattern of temperature and the growing season. Hence, in spring and summer, the value for h for trees is higher than in winter. Agricultural plants like oat, corn or rye need more watering. Thus, these plants show high values for h in the growing season. b) Only temperature and relative humidity at 2 pm are needed as input variables. These can relatively