Clim. Past Discuss., 8, 2853–2892, 2012
www.clim-past-discuss.net/8/2853/2012/
doi:10.5194/cpd-8-2853-2012

Climate
of the Past
Discussions

Reconstruction of drip-water δ^{18}O based on calcite oxygen and clumped isotopes of speleothems from Bunker Cave (Germany)

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Received: 21 June 2012 – Accepted: 6 July 2012 – Published: 24 July 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The geochemical signature of many speleothems used for reconstruction of past continental climates is affected by kinetic isotope fractionation. This limits quantitative paleoclimate reconstruction and, in cases where the kinetic fractionation varies with time, also affects relative paleoclimate interpretations. In carbonate archive research, clumped isotope thermometry is typically used as proxy for absolute temperatures. In the case of speleothems, however, clumped isotopes provide a sensitive indicator for disequilibrium effects. The extent of kinetic fractionation co-varies in Δ_{47} and $\delta^{18}O$ so that it can be used to account for disequilibrium in $\delta^{18}O$ and to extract the past drip-water composition.

Here we apply this approach to stalagmites from Bunker Cave (Germany) and calculate drip-water $\delta^{18}O_w$ values for the Eemian, Marine Isotope Stage (MIS) 3, and the Holocene, relying on independent temperature estimates and accounting for disequilibrium. Applying the co-variation method to modern calcite precipitates yields drip-water $\delta^{18}O_w$ values in agreement with modern cave drip-water $\delta^{18}O_w$ of -7.9 ± 0.3 ‰, despite large and variable disequilibrium effects in both calcite $\delta^{18}O_c$ and Δ_{47}. Reconstructed paleo-drip-water $\delta^{18}O_w$ values are lower during colder periods (e.g., MIS 3: -8.5 ± 0.4 ‰ and the early Holocene at 11 kyr: -9.3 ± 0.1 ‰) and show higher values during warmer climatic periods (e.g., the Eemian: -7.5 ± 0.2 ‰ and the Holocene Climatic Optimum: -7.2 ± 0.3 ‰). This new approach offers a unique possibility for quantitative climate reconstruction including the assessment of past hydrological conditions while accounting for disequilibrium effects.

1 Introduction

Speleothems provide an increasingly popular archive for terrestrial paleoclimate reconstruction, with their oxygen isotope signals recording variations in cave temperature and local rain (e.g., McDermott, 2004; Fairchild and Baker, 2012). The isotopic composition of snow and rain ($\delta^{18}O$, δD) reveal important details about the hydrological cycle such as the source region of water vapour, storm trajectories, and the conditions during vapour condensation and rain-out (Clark and Fritz, 1997; Aggarwal et al., 2005; Lachniet, 2009). The rainfall $\delta^{18}O_w$ values often show a temperature dependence that is particularly pronounced in the mid and high latitudes. The strongest temperature dependence of $\delta^{18}O_w$ was observed in polar stations (0.8–0.9 ‰(°C)$^{-1}$; Dansgaard, 1964; Rozanski et al., 1993). In mid-latitudes moderate values were measured (0.53–0.69 ‰(°C)$^{-1}$; Dansgaard, 1964; Rozanski et al., 1993; Gourcy et al., 2005), whereas low latitudes or marine sites show only a low temperature dependence of 0.17 ‰(°C)$^{-1}$ (Rozanski et al., 1993).

The modern-day spatial temperature dependence of oxygen isotopes in rainfall is commonly used as calibration for paleoclimatic applications, e.g., for polar ice cores (Lorius et al., 1985; Johnsen et al., 1992; Grootes et al., 1993) and speleothems (Duplessy et al., 1970; Dorale et al., 1992) with the aim to reconstruct past temperature changes. The basic assumption for these applications is that the $\delta^{18}O_w$–T relationship is constant over time. However, noble gas studies in groundwater (Loosli et al., 2001; Varsány et al., 2011) suggest that this relationship was different in the past, at least regionally. Similar deviations between the modern spatial $\delta^{18}O_w$–T relationship and the temporal reconstructions were also observed for polar ice-cores by comparison with independent temperature calibrations (Cuffey et al., 1995; Severinghaus et al., 1998). Both examples highlight the significance for an improved understanding of the $\delta^{18}O_w$–T relationship and its temporal variability. This requires reliable reconstruction of both paleotemperature and rainfall isotopes.

Speleothems are the potentially ideal candidates for rainfall $\delta^{18}O_w$ reconstruction due to the possibility of high-precision age determination, high-resolution stable isotope measurements, and their ability to faithfully retain climatic signals (e.g., Gascoyne, 1992; McDermott, 2004; Fairchild and Baker, 2012). Complications arise from disequilibrium effects that often influence $\delta^{18}O_c$ and $\delta^{13}C$ values (Mickler et al., 2006; Demény et al., 2010; McDermott et al., 2011; Tremaine et al., 2011; Riechelmann et al., 2012) and have been recently shown to influence also clumped isotope values (Affek et al., 2008; Meckler et al., 2009; Daëron et al., 2011; Wainer et al., 2011; Kluge and Affek, 2012). Contrary to the early suggestion of a constant disequilibrium offset (in Soreq Cave; Affek et al., 2008), Kluge and Affek (2012) observed in Bunker Cave temporal variations in the degree of kinetic isotope fractionation which preclude the use of constant disequilibrium offsets at least for certain speleothems or in certain caves.

Daëron et al. (2011) proposed an approach that corrects for the disequilibrium and allows to calculate paleotemperatures and paleo-rainfall $\delta^{18}O_w$ values despite kinetic isotope fractionation. Their approach is based on the combined offset in Δ_{47} and $\delta^{18}O$ and is, hence, referred to as co-variation method. As the isotopic disequilibrium in both Δ_{47} and $\delta^{18}O$ is related to rapid CO_2 degassing and as it affects both isotopic tracers, it is assumed that the relationship between them is practically invariant with temperature and is therefore temporally constant (Guo, 2008; Daëron et al., 2011). The co-variance method offers to reconstruct either past temperature or past drip water $\delta^{18}O_w$. It relies on the fixed co-variance relationship between Δ_{47} and $\delta^{18}O$ and knowledge of the difference between drip-water $\delta^{18}O_w$ and calcite $\delta^{18}O_c$ (to reconstruct temperature), or of the difference between measured and expected Δ_{47} (to reconstruct water $\delta^{18}O_w$). The co-variance method was first applied to reconstruct temperatures from a flowstone from Villars Cave (France) using drip-water $\delta^{18}O_w$ determined from speleothems fluid inclusions, resulting in reasonable temperature estimates (Wainer et al., 2011). Here we use the opposite approach to reconstruct $\delta^{18}O_w$ values in paleo-rainfall.

In this study, we present the first paleo-drip-water $\delta^{18}O_w$ record based on the clumped isotope co-variation method. We investigate the reproducibility of the signals, check the overall precision, and the applicability of the method for drip-water $\delta^{18}O_w$ reconstruction by measuring temporally overlapping stalagmites that grew during the last glacial cycle in Bunker Cave (Germany). The potential and limitations of the approach are assessed using modern calcite precipitated in the cave in comparison with monitoring data of Bunker Cave conditions.

2 Study site and samples

Bunker Cave (51° 22′ N, 7° 40′ E) is located in the Middle to Upper Devonian limestone of the Rhenish-Slate Mountains (Germany) at about 180 m a.s.l. and is overlain by 15–30 m of karstified limestone bedrock. The meteorological conditions in the region are dominated by North Atlantic pressure systems, with a temperate climate, precipitation throughout the year (annual mean 900 mm, 1961–1990), and a mean annual air temperature of 9.5 °C (1961–1990). The air temperature in the last two decades has increased to about 10.5 °C (1988–2007, German Meteorological Service DWD), a change that is also observed in the cave temperature. During the cave monitoring period 2006–2011 a mean temperature of 10.8 °C was measured in Bunker Cave. Drip-water $\delta^{18}O_w$ values are rather constant at -7.9 ± 0.3 ‰ for all stalagmite-related monitoring sites within Bunker Cave.

The study uses four stalagmites (BU1, BU2, BU4, BU-UWE) from Bunker Cave that grew through the Holocene (past 8.2 kyr, BU1, BU4), the early Holocene (∼ 11 kyr, BU2, BU-UWE), MIS 3 (BU2, BU-UWE) and the Eemian (BU1, BU-UWE). In addition, calcite that precipitated on watch glasses in three month intervals at different seasons between 2007 and 2011 is used for comparison and as test material for the methodology (Table 1). Further modern material has been sampled from the adjacent Dechen Cave (DC1, DC2), B7 Cave (B7-B-01) and Hüttenbläserschacht Cave (HC1-HC4). All stalagmites from Bunker Cave grew in close proximity to each other: BU1, BU2 and BU4 were about 10 m apart, whereas BU-UWE grew in a narrow passage 20–30 m away.

3 Methods

3.1 Clumped isotopes and measurement procedure

Carbonate clumped isotopes (reported as Δ_{47}) are a measure of the chemical bonding between ^{13}C and ^{18}O in the lattice of a carbonate mineral. Under equilibrium conditions it reflects the carbonate precipitation temperature, thus providing a paleotemperature proxy, with higher Δ_{47} values corresponding to lower temperatures and vice versa (Ghosh et al., 2006; Eiler, 2007, 2011). At typical Earth surface temperatures Δ_{47} is between 0.6 and 0.7 ‰.

The stalagmites were sampled along the growth axis for stable and clumped isotopes (Table 2). Sample preparation, cleaning and mass spectrometric measurements followed the procedures described by Affek and Eiler (2006), Huntington et al. (2009), and Zaarur et al. (2011). In brief, CO_2 was extracted from 4–6 mg of speleothem calcite by overnight reaction with 105 % phosphoric acid at 25 °C. The generated CO_2 gas was purified using a helium-purged GC column. The measurements were done using a dual-inlet gas-source isotope ratio mass spectrometer (Thermo Fisher MAT 253). Several standards (Carrara marble, NBS 19, CO_2 gas equilibrated with H_2O, cylinder CO_2) were measured regularly for inter-laboratory comparison (Dennis et al., 2011).

Stalagmite samples were measured throughout the years 2010 and 2011 in order to avoid systematic errors associated with short-term fluctuations in mass spectrometric and sample preparation parameters. All stalagmite samples and modern speleothems were measured in 5–7 replicates (Tables 1 and 2), with the exception of some modern watch glass calcite precipitates, that could only be measured once due to the limited sample amount. The uncertainty of a single measurement is ±0.02 ‰ (1σ) based on replicate analyses of standard materials (Carrara marble: $\sigma = \pm 0.02$ ‰, NBS 19: $\sigma = \pm 0.03$ ‰, "CornCO_2" – in-house CO_2 gas standard: $\sigma = \pm 0.02$ ‰). Speleothem sample replicates show a slightly lower variability of typically ±0.010 to 0.015 ‰ (1σ). The uncertainty for the mean of the replicate analyses of a specimen is given as standard error (SE). In the case of the single watch glass measurements the uncertainty was assumed to be identical to the 1σ uncertainty of the standards.

Absolute δ^{18}O values were defined using a pre-calibrated Oztech reference gas (Safford, AZ, USA; $\delta^{13}\text{C} = -3.64$ ‰, $\delta^{18}\text{O} = -15.80$ ‰, both at the VPDB scale) and verified by regular measurements of NBS 19. The mean δ^{18}O of the NBS 19 measurements is -2.17 ± 0.04 ‰ (1σ, $n = 13$), in agreement with the NIST reference value of -2.2 ‰. δ^{13}C values are slightly higher (2.10 ± 0.11 ‰, 1σ, $n = 13$) than the NIST reference value of 1.95 ‰. Uncertainties in the δ^{18}O values for replicate samples are given as standard errors. The 1σ-standard deviation is 0.1–0.2 ‰ with typical standard errors of about 0.06 ‰.

3.2 Calculation of δ^{18}O and Δ_{47} values

Δ_{47} is calculated following Affek and Eiler (2006) and Huntington et al. (2009). We use the Δ_{47}–T relationship of Ghosh et al. (2006) as a reference for carbonate samples precipitated in isotopic equilibrium:

$$\Delta_{47,\text{equil}}(T) = 59200/T^2 - 0.02 \ (\Delta_{47} \text{ in ‰}, \ T \text{ in K}) \quad (1)$$

Δ_{47} values are reported using the same reference frame of the original calibration (Ghosh et al., 2006) in which Carrara marble yields a value of 0.352 ‰. In the Supplement (Table S1) we report the speleothem data also using the newly defined absolute reference frame that is determined by CO_2-H_2O equilibration at different temperatures and comparing to absolute values determined theoretically (Wang et al., 2004; Dennis et al., 2011).

The conversion of calcite $\delta^{18}\text{O}_\text{c}$ to drip-water $\delta^{18}\text{O}_\text{w}$ is based on the measured or independently determined temperature, T, and the equilibrium fractionation factor of Kim and O'Neil (1997) with a small correction for the acid reaction fractionation (Böhm et al., 2000; Affek et al., 2008):

$$1000 \ln \alpha_{\text{calcite}-\text{H}_2\text{O}} = 18.03 \cdot 10^3/T - 32.17 \quad (2)$$

Isotopic disequilibrium in Δ_{47} is calculated with respect to the Ghosh et al. (2006) calibration line (Eq. 1). For $\delta^{18}O_c$, the degree of disequilibrium is based on the difference from the expected equilibrium isotope fractionation according to Eq. (2). Calcite $\delta^{18}O_c$ values are reported with respect to VPDB as reference frame, water $\delta^{18}O_w$ values with respect to VSMOW.

3.3 Δ_{47}-$\delta^{18}O$ co-variation method

The basis of the co-variation method is the assumption that the kinetic isotope effect affects Δ_{47} and $\delta^{18}O$ proportionally. Theoretical calculations of kinetic isotope fractionation associated with rapid CO_2 degassing from a calcite-precipitating solution predict $\delta^{18}O$ values to increase whereas Δ_{47} decreases in the dissolved inorganic carbon (Guo, 2008). An empirical study of modern calcite precipitates from Villars Cave in France (Daëron et al., 2011; Wainer et al., 2011) supports this theory. Daëron et al. (2011) observed a correlation between the disequilibrium offsets of both $\delta^{18}O$ and Δ_{47} in speleothems from several caves in the northern and southern mid-latitudes. They found a similar correlation in precipitation experiments that simulated natural stalagmite formation. As the two tracers are linked, the co-variance between them allows to project the data back to zero offset, thus estimating the equilibrium values using the co-variation slope and the offset in $\delta^{18}O$ or in Δ_{47}. This approach, therefore, requires knowledge of either the cave temperature (using an independent temperature estimate for the region) or the $\delta^{18}O$ value of the drip-water ($\delta^{18}O_w$, that can be obtained for example from fluid-inclusion measurements).

Theoretical work suggests that the co-variation slope is practically invariant with temperature (Guo, 2008). However, the slope in Villars Cave was higher than the theoretical prediction (Daëron et al., 2011) raising a question regarding the applicability of this method in different climate regimes. Here, we examine the co-variation slope for a set of mid-latitudinal caves with temperatures of ~ 10 °C and compare them to the warmer Soreq Cave (~ 18 °C; Affek et al., 2008).

Temperature and drip-water $\delta^{18}O_w$ reconstruction

If the $\delta^{18}O_w$ value of the drip-water is known, temperatures can be calculated from the measured calcite $\delta^{18}O_c$, Δ_{47}, and the co-variation slope S (defined as offset Δ_{47} vs. offset $\delta^{18}O$). Details of this approach are given in Daëron et al. (2011) and Wainer et al. (2011). Alternatively, if the cave temperature is known, the drip-water $\delta^{18}O_w$ can be directly calculated from the equilibrium calcite $\delta^{18}O$ value ($\delta^{18}O_{equil}$) via the fractionation factor $\alpha(T)$ (Eq. 2), following a co-variation calculation of $\delta^{18}O_{equil}$.

$\delta^{18}O_{equil}$ can be determined from the offset in Δ_{47} ($\Delta_{47,equil}$ is derived from Eq. 1 and the cave temperature), the measured calcite $\delta^{18}O$ ($\delta^{18}O_{measured}$) and the co-variation slope S:

$$\delta^{18}O_{equil}=\delta^{18}O_{measured}+(\Delta_{47,equil}-\Delta_{47,measured})\cdot\frac{1}{S} \qquad (3)$$

Here we use independent temperature estimates for the different time windows of stalagmite growth (Table 2). For the last 2 kyr, we use the mean of the two multi-proxy reconstructions ("CPS" and "EIV") of Mann et al. (2008) calculated for the growth period of each sample in order to derive the deviation from the modern-day temperature. "CPS" (composite plus scale) and "EIV" (error in variables) refer to reconstructions based on multiple proxies (e.g., tree rings, corals, ice cores, lacustrine and marine sediments, speleothems, and historical documents), which are standardized and combined to form a regional or hemispheric mean. We calculate the temperature variations around a reference temperature of the 1961–1990 local mean of 9.5 °C.

Some of the Holocene Bunker Cave stalagmites were analysed for their fluid inclusion noble gas composition in order to derive temperatures based on the noble gas solubility (Kluge et al., 2008; and see below). In cases where noble gas temperatures (NGTs) are available for the same time windows as the clumped isotope samples we used these temperatures (Table 3) as the basis for the $\delta^{18}O_w$ reconstruction. If no NGTs are available for a certain time window we use pollen-based temperature records for Central-Western Europe (Davis et al., 2003). In particular, MIS 3 paleotemperature estimates are derived from pollen spectra in the La Grande Pile sediment core from North-Eastern France (Guiot et al., 1989). For the Eemian we use the mean of several studies, such as pollen data from Western and Central Europe (Guiot et al., 1989; Zagwijn, 1996; Klotz et al., 2003), the coupled atmosphere-ocean general circulation model ECHO-G (Felis et al., 2004), and a global climate model linked to paleoclimate data and a dynamic ice-sheet model (Otto-Bliesner et al., 2006).

3.4 Noble gas measurement and evaluation

For analysis of noble gas concentrations in fluid inclusions, cubes of 0.5–1.4 g were sampled close to the growth axis of stalagmite BU1, and 1.0–2.7 g for stalagmite BU-UWE. Gas extraction and analysis followed the procedures described in Kluge et al. (2008). In brief, the cubes were placed in a stainless steel crusher, pumped overnight at room temperature while the crusher itself was heated (70–150 °C), and then crushed. The released water and noble gas amount was determined for each extraction step. The noble gases were purified and separated prior to sequential admission to a static sector-field mass spectrometer (MM 5400). NGTs were determined by inverse modeling of the noble gas concentrations in the inclusion water, using the method introduced by Aeschbach-Hertig et al. (1999). This calculation uses the temperature-dependence of the noble gas solubility with higher noble gas concentrations at lower temperatures and accounts for air from air-filled inclusions (details in Supplement).

NGTs are reproducible to ±1.3 °C for BU1 and to ±0.7 °C for the early Holocene part of BU-UWE, but all show consistently lower temperatures compared to the 1961–1990 reference (Kluge et al., 2008). There are several possible causes for offsets in speleothems fluid-inclusion noble-gas concentrations (Scheidegger et al., 2010, 2011). For a first-order correction, we assume that the offset in stalagmites BU1 and BU-UWE was constant over time. By comparing the NGTs for the last 2 kyr to the independently reconstructed late Holocene temperatures (Mann et al., 2008) and anchoring them to the regional 1961–1990 temperature reference, we derive an offset of the NGTs of 2.2 ± 0.5 °C. All NGTs were corrected using this constant offset. The resulting Holocene mean NGT is 10.1 ± 1.4 °C, in agreement with the modern-day air-temperature (9.5 °C during 1961–1990 and the more recent value of 10.5 °C during 1988–2007).

3.5 Error analysis

Uncertainties in the reconstructed drip-water $\delta^{18}O_w$ values arise from analytical errors in Δ_{47} and $\delta^{18}O$, the estimated temperatures, the co-variation slope, and the equilibrium Δ_{47}–T calibration relationship. For calculating the drip-water $\delta^{18}O_w$ values, the analytical errors in Δ_{47} and $\delta^{18}O$ were propagated together with the uncertainty in the temperatures and in the co-variation slope using Gaussian error propagation. In case of the NGTs, the uncertainty based on measurement and inverse modelling of the noble gas concentrations together with the uncertainty in the offset correction was used. For paleotemperatures obtained from literature data an uncertainty of 1 °C was assumed. The temperature uncertainty was taken into account in the conversion of calcite $\delta^{18}O_c$ into the corresponding drip-water $\delta^{18}O_w$. The uncertainty of the equilibrium Δ_{47}–T relationship has not been considered.

4 Results

4.1 Clumped isotope thermometry

The Δ_{47} values of the modern calcite deposits ($n = 15$, Table 1) are between 0.638 and 0.689 ‰, those of the Holocene stalagmite samples ($n = 18$, Table 2) between 0.659 and 0.705 ‰. The Δ_{47} values of the early Holocene samples ($n = 5$, ~ 11 kyr) range from 0.663 and 0.674 ‰, those of the MIS3 samples ($n = 3$, ~ 53 kyr) are between 0.692 and 0.702 ‰, and those of the Eemian samples ($n = 4$, 120–130 kyr) are between 0.662 and 0.676 ‰. The expected equilibrium Δ_{47} values are all significantly higher: 0.713–0.726 ‰ for the Holocene and the Eemian (8.5–11 °C), 0.745 ‰ for the early Holocene samples (~ 5 °C), and 0.751 ‰ for the MIS 3 samples (~ 4 °C).

Temperatures calculated based on the equilibrium Δ_{47} calibration are, thus, too high for all growth periods, due to Δ_{47} values that are too low. The deviation in temperature spans a large range of values in Holocene and modern samples (4–16 °C), reflecting variations in the degree of kinetic isotope fractionation (Kluge and Affek, 2012).

4.2 Calcite oxygen isotope composition

Calcite $\delta^{18}O_c$ values vary between −6.4 and −4.7 ‰ and show for all modern and Holocene speleothems elevated $\delta^{18}O_c$ values (+0.3 to +1.7 ‰) compared to the values expected for equilibrium precipitation at the estimated temperature and the modern drip-water $\delta^{18}O_w$ of −7.9 ‰. The enrichment in the modern speleothems is +0.9 ± 0.4 ‰ ($n = 15$), ranging from +0.3 ‰ to +1.4 ‰. The enrichment in the Holocene stalagmites is similar, with values between +0.4 ‰ to +1.7 ‰, averaging +1.0 ± 0.3 ‰ ($n = 18$).

4.3 Δ_{47}-$\delta^{18}O$ co-variation slope

In order to account for kinetic isotope fractionation effects and to project the observations back to the equilibrium calcite $\delta^{18}O_c$ values, the co-variance slope between the offsets in $\delta^{18}O$ and Δ_{47} is required. Guo (2008) used ab-initio transition state theory to calculate co-variation slopes that vary between −0.017 and −0.026 (namely, 0.017 to 0.026 ‰ decrease in Δ_{47} per 1 ‰ increase in $\delta^{18}O$, with the variability depending on the pathway of CO_2-degassing and only weakly on temperature). Empirical data yield a higher sensitivity of Δ_{47} with respect to $\delta^{18}O$, resulting in a steeper slope. Co-variance slopes of −0.04 and −0.06 were observed for speleothems from caves at mid-latitudes with temperatures between 4 and 13 °C (Daëron et al., 2011; Wainer et al., 2011). Clumped and oxygen isotope measurements in Bunker Cave yield similar results (Figs. 1, 2). Calcite precipitated on watch glasses at 11–12 °C results in a slope of -0.055 ± 0.002 ($n = 7$), modern speleothems from adjacent caves yield -0.046 ± 0.007 ($n = 8$), and the combined fit of all modern speleothems results in slope of -0.047 ± 0.005 ($n = 15$, Fig. 1). Holocene speleothem offsets, that were calculated assuming constant temperature and drip-water $\delta^{18}O_w$ values that are identical to the modern values, follow the same Δ_{47}-$\delta^{18}O$ co-variance as in modern cave calcite (Fig. 2). We therefore use the combined slope of all modern data as basis for the reconstruction of past $\delta^{18}O_w$.

Results from Soreq Cave (Israel) suggest that the co-variation slope might be independent from temperature. In this cave, one modern stalagmite sample that grew at 18 °C yielded a slope of -0.057 ± 0.067 (Affek et al., 2008), similar to the results of speleothems from mid-latitudes. As all Bunker Cave samples grew at a limited temperature range (similar to Villars Cave, France; Daëron et al., 2011; Wainer et al., 2011) we base our calculations on the slope determined from modern Bunker Cave speleothems (−0.047) and neglect the possible minor temperature dependence of the co-variation slope. In general, the reconstructed $\delta^{18}O_w$ values are not sensitive to small variations in the slope (see sensitivity test below).

4.4 Sensitivity of the co-variation slope

Theoretical calculations suggest that the slope becomes steeper (more negative) at lower temperature (Guo, 2008), albeit, with a very weak temperature dependence of $0.0001\ (^{\circ}C)^{-1}$. In order to investigate the influence of small variations in the co-variation slope on the resulting rainfall $\delta^{18}O_w$, a sensitivity analysis was performed using a slope of −0.047 for a mean offset of 1 ‰ in calcite $\delta^{18}O_c$ (Fig. 3). The offset of 1 ‰ in $\delta^{18}O_c$ is a typical value for speleothems from numerous caves (McDermott et al., 2011) and is identical to the mean observed in Bunker Cave. A lower offset in calcite $\delta^{18}O_c$ (dashed line in Fig. 3) reduces the sensitivity of the calculated drip-water $\delta^{18}O_w$ on the co-variation slope, whereas a higher offset (dotted line) increases it.

We allow the co-variation slope to vary by ±0.005 around the mean value of −0.047, resulting in deviations of less than 0.15 ‰ in the calculated $\delta^{18}O_w$. Significantly steeper slopes lead only to small changes in reconstructed $\delta^{18}O_w$, e.g., 0.2 ‰ at a slope of −0.057. Thus, the sensitivity analysis indicates that minor changes in the slope, as suggested by the weak temperature dependence inferred from theoretical calculations, have negligible influence on the calculated drip-water $\delta^{18}O_w$ values. Significantly lower slopes (such as −0.03), on the other hand, would result in higher sensitivity of $\delta^{18}O_w$ to the uncertainty in the slope.

4.5 Drip-water $\delta^{18}O_w$ reconstruction using independent temperature estimates

Drip-water $\delta^{18}O_w$ values are estimated using Eq. (3), the co-variation slope of −0.047, and paleotemperatures from independent studies (Table 2). The reconstructed drip-water $\delta^{18}O_w$ varies between −6.7 and −9.5 ‰ (Tables 1, 2). The lowest values are found in the early Holocene with a mean value of −9.3 ± 0.1 ‰ ($n = 5$), the highest values are observed in the mid-Holocene (5–8 kyr) with a mean value of −7.2 ± 0.3 ‰ ($n = 5$), and in the Eemian with a mean of −7.5 ± 0.2 ‰ ($n = 4$). Holocene values, averaging −7.6 ± 0.4 ‰ ($n = 18$), are close to the mean drip-water $\delta^{18}O_w$ value of −7.9 ± 0.3 ‰ (Fig. 4). Despite the similarity of the Holocene mean to the modern value, a trend of decreasing drip-water $\delta^{18}O_w$ values is observed from the mid-Holocene towards today (Fig. 4). This trend is interrupted in the last 2 kyr by increased variability. MIS 3 values with an average of −8.5 ± 0.4 ‰ ($n = 3$) are intermediate between the more negative values observed at the beginning of the Holocene at 11 kyr and the higher values for climatic optimum periods (mid-Holocene: 6–8 kyr, Eemian). Typical uncertainties in the calculated drip-water $\delta^{18}O_w$ values are 0.3 ‰.

5 Interpretation and discussion

All stalagmite Δ_{47} values clearly plot below the equilibrium Δ_{47}–T relationship indicating that they are all affected by disequilibrium effects. This is supported by the calcite $\delta^{18}O_c$ data showing higher values than expected at isotopic equilibrium. In contrast to early assumptions (Affek et al., 2008) the extent of kinetic offset cannot be assumed a priori to be constant; at least in some caves it varies spatially and possibly also temporally (in Bunker Cave, Δ_{47} values vary by ~0.04 ‰ in two Holocene stalagmites; Kluge and Affek, 2012). There are three parameters that affect calcite $\delta^{18}O_c$ values – drip water $\delta^{18}O_w$, cave temperature, and the degree of disequilibrium – making it impossible to determine both paleotemperatures and drip-water $\delta^{18}O_w$ directly from speleothem calcite $\delta^{18}O_c$. The co-variation between Δ_{47} and $\delta^{18}O$ provides the possibility to quantify the kinetic offset in order to calculate $\delta^{18}O_w$.

5.1 Co-variation reconstruction of drip-water $\delta^{18}O_w$ values

In order to test the applicability of the co-variation method for drip-water reconstruction in Bunker Cave we focus first on the modern calcite precipitates. We divide the modern calcites into two sub-sets, whereof one is used to calculate the co-variation slope, which is then applied to the second group as a test. Calculated drip-water $\delta^{18}O_w$ values are -7.7 ± 0.2 ‰ ($n = 7$) for the Bunker Cave watch glasses based on the slope of other modern precipitates (−0.046), and -7.6 ± 0.2 ‰ ($n = 8$) for the modern calcites from Bunker Cave, B7 Cave, Dechen Cave and Hüttenbläserschacht Cave using the slope calculated from the watch glasses (−0.055). Both values agree with the mean value of modern drip-water of -7.9 ± 0.3 ‰. The agreement of the co-variation $\delta^{18}O_w$ values in both sub-sets is remarkable since the kinetic isotope fractionation in the modern speleothems is highly variable (Fig. 1) with offsets in $\delta^{18}O_c$ ranging from 0.3 to 1.4 ‰ and with corresponding Δ_{47} offsets of −0.032 to −0.075 ‰. The good agreement between measured and calculated drip-water values in modern speleothems implies that the co-variation method is applicable for the Bunker Cave system; we therefore follow the approach of Wainer et al. (2011) in applying it to older speleothems, assuming the co-variance slope to be constant over time.

The reconstructed Holocene drip-water $\delta^{18}O_w$ values vary between −6.7 and −8.3 ‰ with an evolution that can be divided in two phases: a trend towards lower values from ~ 7.5 to 2 kyr, and a rather variable phase during the last 2 kyr with significant fluctuations (Table 2, Fig. 4).

5.1.1 Late Holocene drip-water $\delta^{18}O_w$ values

Most samples from the last 2 kyr (Fig. 4) show $\delta^{18}O_w$ values that are close to the mean $\delta^{18}O_w$ value of recent drip-water (−7.9 ± 0.3 ‰). Two periods stand out with drip-water $\delta^{18}O_w$ that are either more positive at 0.9 kyr (−7.0 ± 0.3 ‰) or more negative at 1.2–1.3 kyr (−8.3 ± 0.1 ‰, $n = 2$) relative to today. Due to the limited number of data points we do not attempt to interpret this part of the drip-water $\delta^{18}O_w$ record, but note that high resolution data at this time period may reveal an interesting signal. Other records such as the rainfall $\delta^{18}O_w$ reconstruction from Lake Ammersee (450 km SE of Bunker Cave; von Grafenstein et al., 1999) show a variability of 1 ‰ during the last 2 kyr, consistent with our observations (Fig. 4).

5.1.2 Holocene drip-water $\delta^{18}O_w$ values

During the Holocene a general trend of decreasing drip-water $\delta^{18}O_w$ values is observed from 7.5 kyr (−7.1 ‰) to 2 kyr (−7.6 ‰; Fig. 4). This trend follows the summer insolation at high northern latitudes (65° N) that is decreasing from its maximum at 9–10 kyr. This trend is similar to that observed in the NGRIP ice core $\delta^{18}O$ (NGRIP members, 2004), that is most enriched at about 8 kyr and decreases by ~ 0.6 ‰ until 2 kyr (Fig. 4). Although Greenland is rather remote from Western Germany, the similarity in the rainfall (or drip-water) $\delta^{18}O_w$ trends may be related to a common cause such as changes in insolation or major atmospheric circulation patterns (Wanner et al., 2008).

During the Holocene Climatic Optimum (~ 6–8 kyr), when insolation was close to its maximum, higher paleotemperatures were observed in several proxy records in Central and Northern Europe (Seppä and Birks, 2001; Verschuren et al., 2004) and the Norwegian Sea (Calvo et al., 2002). Noble gas temperatures from stalagmite BU1 (Table 3) are higher during this time period compared to the rest of the Holocene. This temperature difference can explain at least part of the observed trend in the drip-water $\delta^{18}O_w$ values, reflecting the temperature dependence of rainfall $\delta^{18}O_w$ in mid and high latitudes being enriched in ^{18}O at higher temperatures (Rozanski et al., 1993).

The $\delta^{18}O_w$ evolution derived from the Bunker Cave stalagmites is consistent with an independent water $\delta^{18}O_w$ record based on ostracods from Lake Ammersee in Southern Germany (von Grafenstein et al., 1999), that also shows a decrease by 0.4 ‰ from 6–8 kyr towards the late Holocene (Fig. 4).

5.1.3 Drip-water $\delta^{18}O_w$ values in the early Holocene and MIS 3

Drip-water $\delta^{18}O_w$ values in the early Holocene (~ 11 kyr) are the lowest of the whole record (–9.3 ± 0.1 ‰, $n = 5$, Fig. 4), ca. 1.7 ‰ lower than the Holocene mean value. Also the MIS 3 stalagmites (~ 53 kyr) yield low $\delta^{18}O_w$ values of –8.5 ± 0.4 ‰ ($n = 3$). Even lower values may be expected during peak glacial periods such as MIS 2 and the Last Glacial Maximum (LGM), but unfortunately no stalagmites from these periods are available from Bunker Cave, probably as a result of freezing bedrock temperatures.

Our observations of very negative early Holocene and MIS 3 $\delta^{18}O_w$ values are consistent with several independent reconstructions of rainfall $\delta^{18}O_w$ in the region, including lake sediments, tooth enamel, and fossil groundwater. Lake water $\delta^{18}O_w$ values reconstructed from Lake Ammersee sediment are depleted by up to 4.7 ‰ at the end of the last Glacial (15.5 kyr) relative to the Holocene, and depleted by 3.1 ‰ during the Younger Dryas at ~ 12 kyr (von Grafenstein et al., 1999), with early Holocene $\delta^{18}O_w$

values moderately low (up to 1 ‰ depletion at 11 kyr). Mammoth tooth enamel independently confirms our $\delta^{18}O_w$ estimate of −8.5 ‰ during MIS 3. The enamel-based estimates of mid to late Weichselian (52–24 kyr) rainfall $\delta^{18}O_w$ values are −9 ‰ to −10 ‰ for the Bunker Cave region (Arppe and Karhu, 2010), or −8.4 to −10.1 ‰ for the German Rhine River area (Tütken et al., 2008). Glacial paleogroundwater $\delta^{18}O_w$ values in Western and Central Europe are about 1–1.5 ‰ more negative than modern infiltration (Loosli et al., 2001) with maximum differences between present-day and late Pleistocene (20–40 kyr) groundwater $\delta^{18}O_w$ values of 2.5–3 ‰ (Darling, 2004). The negative drip-water $\delta^{18}O_w$ values that we observe for MIS 3 Bunker Cave stalagmites are, thus, well within the range of groundwater data. The drip-water $\delta^{18}O_w$ variation reconstructed from the early Holocene stalagmites is slightly more pronounced than in the Lake Ammersee record (von Grafenstein et al., 1999), but of similar magnitude as found in paleogroundwater from Southern Germany (Darling, 2004).

Relatively low continental rainfall $\delta^{18}O_w$ values despite elevated ocean water $\delta^{18}O_w$ values may be explained by a steeper sea-to-land temperature gradient with a larger continental glacial to interglacial temperature amplitude than at the sea surface. Temperatures in the Atlantic were on average lower by 2.6 ± 2.0 °C during the LGM compared to the Holocene (60° N–60° S, MARGO project members, 2009). In contrast, temperatures in Central Europe were lower by more than 9 °C (Blaser et al., 2010; Varsány et al., 2011).

Another indication for a steeper gradient comes from a stalagmite-based study (McDermott et al., 2011) that observed a significant increase in the longitudinal isotopic gradient within Europe during the early Holocene as compared to the late Holocene. The distance from the Irish coast to Bunker Cave is roughly 15° longitude. Using the gradients of McDermott et al. (2011) as a guide, we obtain a longitudinal difference in rainfall $\delta^{18}O_w$ values of −3.3 ‰ for the early Holocene (−0.22 ‰/° longitude) and −1.8 ‰ for the late Holocene (−0.12 ‰/° longitude). This difference of about 1.5 ‰ is consistent with the relative drip-water $\delta^{18}O_w$ change of 1.7 ± 0.4 ‰ between these two periods in the Bunker Cave record.

5.1.4 Drip-water $\delta^{18}O_w$ values in the Eemian

The temperature inferred for the Eemian is slightly higher (+1.5 °C) than the 1961–1990 reference value, and is close to the recent air-temperature mean of 10.5 °C (1988–2007). Using this temperature for the Δ_{47}-$\delta^{18}O$ co-variation approach yields Eemian drip-water $\delta^{18}O_w$ values that are within the range of the Holocene values (–7.2 to –7.7 ‰; Fig. 4). The mean Eemian drip-water $\delta^{18}O_w$ value of -7.5 ± 0.2 ‰ ($n = 4$) is indistinguishable from the Holocene mean (-7.6 ± 0.4 ‰) and close to the values from the ongoing cave monitoring (-7.9 ± 0.3 ‰). Therefore, the hydrological conditions during the Eemian were probably similar to those of the Holocene.

5.2 Temporal drip-water $\delta^{18}O_w$–temperature relationship

The pioneering studies of Dansgaard (1953), Epstein and Mayeda (1953) and Friedman (1953) examined oxygen isotopes in rain and snow, showing a temperature dependence of $\delta^{18}O_w$ values in precipitation water. Following these studies, $\delta^{18}O_w$–T relationships based on spatial patterns were used for paleoclimatic reconstruction. Applying the modern $\delta^{18}O_w$–T relationship to the past relies on the assumption that spatial patterns can be transcribed into temporal changes; this, however, is uncertain. For example, borehole temperatures from Greenland indicate that the $\delta^{18}O_w$–T relationship was much weaker during the glacial (0.30 ‰(°C)$^{-1}$) compared to the modern relationship (0.67 ‰(°C)$^{-1}$; Johnsen et al., 1992) resulting in an underestimated temperature variability (Cuffey et al., 1995; Dahl-Jensen et al., 1998). Furthermore, $\delta^{18}O_w$–T relationships determined from seasonal data of single stations may deviate from the spatial relationship (Rozanski et al., 1992) and complicate its general application.

The Δ_{47}-$\delta^{18}O$ co-variation method in speleothems offers a new possibility for the reconstruction of drip-water $\delta^{18}O_w$ values and enables an investigation of its temporal relationship with temperature. For a quantitative interpretation of the drip-water $\delta^{18}O_w$ values prior to the Holocene, the ice-volume effect on the seawater $\delta^{18}O_w$ values and therefore the rainfall vapor source has to be taken into account. At times of maximum ice extent, such as during the LGM, seawater was enriched by 1.0 ± 0.1 ‰ (Schrag et al., 2002), during MIS 3 by 0.5–0.8 ‰ (Sowers et al., 1993), by 0.4 ‰ in the Younger Dryas (Arppe and Karhu, 2010), and by 0–0.4 ‰ in the early Holocene. The relative depletion in early Holocene and MIS 3 rainfall, as reflected in Bunker Cave drip water, with respect to later parts of the Holocene is therefore even larger when considering the more enriched water vapor source during these time periods, resulting in a larger effective discrimination against ^{18}O in Western Germany rainfall in the early Holocene and MIS 3.

Within the Holocene we compare the temperature and drip-water $\delta^{18}O_w$ values of the Holocene Climatic Optimum at 7–8 kyr (11.1 ± 1.0 °C, −7.1 ± 0.5 ‰) to the late Holocene at 2–4 kyr (9.5 ± 1.0 °C, −7.6 ± 0.2 ‰), yielding a $\delta^{18}O_w$–T slope of 0.4 ± 0.4 ‰(°C)$^{-1}$. We obtain similar values when we compare the early Holocene at 11 kyr to modern values (0.4 ± 0.1 ‰(°C)$^{-1}$, using an early Holocene ice-volume correction of 0.2 ± 0.2 ‰). Based on the differences between MIS 3 (ice-volume correction 0.65 ± 0.15 ‰) and modern-day temperature and drip-water $\delta^{18}O_w$ values, the $\delta^{18}O_w$–T slope is slightly lower (0.2 ± 0.1 ‰(°C)$^{-1}$). The large uncertainties are due to the small range of temperatures and therefore preclude a more detailed interpretation. The $\delta^{18}O_w$–T slope derived for the period MIS 3 to modern is less steep than for the modern spatial slope observed in European rainfall (0.58 ‰(°C)$^{-1}$), but is consistent with results obtained from paleogroundwater, using noble-gas recharge temperatures and water $\delta^{18}O_w$. For example, Varsány et al. (2011) estimated a slope of 0.38 ‰(°C)$^{-1}$ for Hungary, similar to a European mean value for paleogroundwater of 0.35 ‰(°C)$^{-1}$ (Loosli et al., 2001). The groundwater studies provide robust information on the recharge temperature, but have limited resolution due to the signal dispersion in the aquifer. The application of the co-variation method to speleothems may provide temporally well-resolved information about the evolution of drip-water and rainfall $\delta^{18}O_w$ values. Sufficient sampling of stalagmites of similar ages may reduce the uncertainties and eventually enable a precise assessment of the $\delta^{18}O_w$–T relationship on a temporal scale.

5.3 Water versus speleothem calcite $\delta^{18}O_c$ variability

The $\delta^{18}O_c$ signature of speleothem calcite is influenced by external, climatic parameters, and internal factors associated with kinetic isotope fractionation during degassing of CO_2 from the precipitating solution (Scholz et al., 2009; Mühlinghaus et al., 2009; Dreybrodt and Scholz, 2011). As the degree of kinetic isotope fractionation can vary during speleothem growth (Kluge and Affek, 2012), it is impossible to determine reliable climate parameters based on a single stalagmite, and non-equilibrium processes should be constrained via comparison of several time-overlapping stalagmites by way of replication test (Dorale and Liu, 2009). Whereas isotopic disequilibrium is easily identified in clumped isotopes, it is important to account for its effects also in the interpretation of $\delta^{18}O_c$ values. Even if only the relative variability of the $\delta^{18}O_c$ signal is interpreted, the changing degree of isotopic disequilibrium may affect the signal. Large fluctuations, on the order of several per mil (such as typically observed during deglaciations or the transition between stadials and interstadials), are large enough so that subtle variability around the ~ 1 ‰ disequilibrium offset are likely insignificant. Smaller variations, on the other hand, must be interpreted with caution as they may reflect changes in the degree of kinetic isotope fractionation, possibly following changes in the soil to cave CO_2 concentration gradient (Mühlinghaus et al., 2009; Kluge and Affek, 2012), instead of real drip-water $\delta^{18}O_w$ variability.

The Holocene stalagmites from the Bunker Cave region provide an example of the importance of accounting for variability in the kinetic isotope fractionation. Stalagmite B7-7 from B7 Cave (Niggemann et al., 2003a) and stalagmite AH1 from Atta Cave (Niggemann et al., 2003b) show a trend of decreasing calcite $\delta^{18}O_c$ values from the mid-Holocene towards the present with an amplitude of 0.5–0.7 ‰. The amplitude observed in these records is comparable to the drip-water composition we derived from stalagmites BU1 and BU4 using the co-variation method. However, this trend in calcite $\delta^{18}O_c$ values is not always observed in other stalagmites from the same region and time periods. For instance, stalagmite B7–5 from B7 Cave (Niggemann et al., 2003a) and stalagmites BU4 (Fig. 5) and BU1 (Fohlmeister et al., 2012) from Bunker Cave exhibit no long-term trend. This discrepancy probably reflects variations in the degree of kinetic isotope fractionation in these stalagmites. For example, stalagmite BU4 is affected by a variable degree of kinetic isotope fractionation (Kluge and Affek, 2012) with a reduced offset in the mid-Holocene compared to the late Holocene, corresponding to a shift in $\delta^{18}O_c$ of about 0.5 ‰ (see inset in Fig. 5). Changes in the isotopic disequilibrium can mask subtle climatic signals or create variability in calcite $\delta^{18}O_c$ values that does not exist in the drip water. The co-variation method enables to extract the actual drip-water signals in both cases.

5.4 Potential and limitations of the co-variation method

The co-variation method is only weakly sensitive to the exact value of the co-variation slope and, therefore, to the potential influence of temperature. Theoretical calculations suggest the co-variation slope to be almost invariant with temperature (Guo, 2008), although the precise determination of the slope is strongly influenced by the uncertainties in the expected equilibrium values (i.e., either on the estimate of temperature or drip-water $\delta^{18}O_w$). Our sensitivity analysis (see Sect. 4.4 and Fig. 3) shows this to be of only minor importance for the reconstruction of $\delta^{18}O_w$ at the temperature range of speleothem growth (0–30 °C).

The accurate reconstruction of either paleotemperatures or past drip-water $\delta^{18}O_w$ values via the co-variation method in speleothems requires the knowledge of one of these parameters. A Δ_{47}-$\delta^{18}O$ kinetic isotope fractionation slope of ~ -0.047, as observed here, implies that the uncertainty in temperature translates to a rather large uncertainty in the reconstructed drip water $\delta^{18}O_w$ values. For example, a temperature estimate that is 1 °C too high or too low results in an error of 0.30–0.35 ‰ in the calculated drip-water $\delta^{18}O_w$ value.

The independent information required for the reconstruction can be obtained either through the $\delta^{18}O_w$ values in speleothem fluid inclusions (Wainer et al., 2011) to enable temperature reconstruction, or through independent paleotemperature estimates for drip and rainwater $\delta^{18}O_w$ reconstruction (this study). Temperatures derived from noble gas concentrations in speleothem fluid inclusions can be most useful in that respect, as they are derived from the same stalagmite (Kluge et al., 2008; Scheidegger et al., 2011). As kinetic isotope fractionation effects are widespread (Mickler et al., 2006; McDermott et al., 2011; Tremaine et al., 2011; Riechelmann et al., 2012), fluid-inclusion analysis only provide reliable paleotemperatures in combination with an adequate tool that accounts for kinetic isotope fraction, such as provided by clumped isotope measurements.

6 Conclusions

The combined analysis of Δ_{47} and $\delta^{18}O_c$ values in stalagmite calcite enables the empirical investigation of kinetic isotope fractionation effects in speleothems. It offers new possibilities for quantitative paleoclimate reconstruction that account for these disequilibrium effects via the co-variation method.

The application of the co-variation method is based on the correlated isotopic disequilibrium in Δ_{47} and $\delta^{18}O_c$ with a co-variation slope of −0.047 ‰ offset in Δ_{47} per 1 ‰ offset in $\delta^{18}O$. Although comparable slopes were observed in other mid-latitudinal caves and only a small temperature-dependence was inferred in theoretical models, the slope may vary among cave systems and should be assessed using modern in-situ precipitated calcite. Note, however, that the reconstructed $\delta^{18}O_w$ is only weakly sensitive to the exact slope value.

In this study, we reconstruct past drip-water $\delta^{18}O_w$ values for Bunker Cave (Germany) using independent temperature estimates. Although the stalagmites generally differ in the degree of kinetic isotope fractionation, they yield similar reconstructed drip-water $\delta^{18}O_w$ values. Drip-water $\delta^{18}O_w$ values are most negative during colder periods (MIS 3: −8.5 ± 0.4 ‰, transition from the Younger Dryas to the Holocene: −9.3 ± 0.1 ‰) and are close to modern-day values during the Eemian (−7.5 ± 0.2 ‰) and most of the Holocene (−7.6 ± 0.4 ‰). In summary, the co-variation method is a powerful tool that enables to overcome limitations caused by ubiquitous disequilibrium effects in speleothems, to correct for them and to quantitatively assess the temporal variation of paleoclimatic parameters.

Supplementary material related to this article is available online at: http://www.clim-past-discuss.net/8/2853/2012/cpd-8-2853-2012-supplement.pdf.

Acknowledgements. The research was funded by the German Science Foundation (DFG, Forschungsstipendium KL2391/1-1 to T. Kluge, AE 93/3 to W. Aeschbach-Hertig) and the National Science Foundation (NSF-EAR-0842482 to H. Affek). We are grateful for samples provided by Stefan Niggemann and thank the caving club Letmathe for field assistance.

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Table 1. Clumped isotope Δ_{47}, calcite $\delta^{18}O_c$ (VPDB) and reconstructed dripwater $\delta^{18}O_{w,co-var}$ (VSMOW) of modern calcite precipitates from Bunker Cave and adjacent caves (BU = Bunker Cave, DC = Dechen Cave, HC = Hüttenbläserschacht Cave, B7 = B7 Cave). Samples labelled U are precipitates on watch glasses from Bunker Cave. T is either the in-situ monitoring temperature or the 1961–1990 ambient air-temperature mean (labelled with *).

Sample	T (°C)	replicates	Δ_{47} (‰)	$\delta^{18}O_c$ (‰)	$\delta^{18}O_{w,co-var}$ (‰)
DC-1	10.6	7	0.648 ± 0.005	−5.79 ± 0.07	−7.9 ± 0.3
DC-2	10.6	7	0.657 ± 0.004	−5.64 ± 0.03	−7.5 ± 0.3
HC-1	9.5*	5	0.674 ± 0.004	−6.08 ± 0.03	−8.0 ± 0.3
HC-2	9.5*	5	0.687 ± 0.004	−5.81 ± 0.02	−7.4 ± 0.3
HC-3	9.5*	5	0.671 ± 0.002	−5.39 ± 0.09	−7.4 ± 0.3
HC-4	9.5*	5	0.689 ± 0.001	−6.14 ± 0.03	−7.7 ± 0.2
B7-B0 1	9.4	5	0.668 ± 0.006	−5.85 ± 0.02	−7.9 ± 0.3
U I-4	10.7	1	0.668 ± 0.020	−6.33 ± 0.25	−8.0 ± 0.6
U I-16	11.1	7	0.665 ± 0.008	−6.12 ± 0.02	−7.7 ± 0.3
U IV-15	10.4	1	0.638 ± 0.020	−5.52 ± 0.20	−7.9 ± 0.6
U VII-5	11.1	1	0.670 ± 0.020	−6.38 ± 0.36	−7.8 ± 0.6
U VII-8	11.3	1	0.653 ± 0.020	−5.66 ± 0.20	−7.4 ± 0.5
U VII-14	12	1	0.675 ± 0.020	−6.26 ± 0.20	−7.3 ± 0.5
U VII-15	11.3	4	0.658 ± 0.003	−5.86 ± 0.03	−7.5 ± 0.3
BU4-1	9.5*	5	0.668 ± 0.007	−5.57 ± 0.14	−7.6 ± 0.3

Table 2. Clumped isotope Δ_{47}, calcite $\delta^{18}O_c$ (VPDB) and reconstructed drip-water $\delta^{18}O_{w,co-var}$ (VSMOW) in Bunker Cave stalagmites. "Distance from top" refers to the sample position with respect to the top of the stalagmite. Ages are the result of an age model based on U-Th measurements (Fohlmeister, 2012; ages marked with an asterisk refer to unpublished data). T_{used} is the independent temperature estimate derived from different sources and independent studies.

Sample	Distance from top (mm)	Age (ka)	replicates	Δ_{47} (‰)	$\delta^{18}O_c$ (‰)	$\delta^{18}O_{w,co-var}$ (‰)	T_{used} (°C)
Stalagmite BU1							
BU1-1	15–19	0.70 ± 0.06	5	0.659 ± 0.007	−5.59 ± 0.01	−7.9 ± 0.3	9.3[a]
BU1-2	52–55	1.00 ± 0.15	5	0.673 ± 0.002	−5.70 ± 0.06	−7.7 ± 0.3	9.4[a]
BU1-3	84–86	1.23 ± 0.01	7	0.670 ± 0.009	−6.30 ± 0.02	−8.3 ± 0.3	9.3[a]
BU1-4	137–140	1.40 ± 0.15	5	0.685 ± 0.002	−5.90 ± 0.04	−7.6 ± 0.3	9.3[a]
BU1-5	249–251	4.5 ± 0.5*	5	0.676 ± 0.005	−5.80 ± 0.12	−7.7 ± 0.3	9.4[b]
BU1-6	347–351	5.04 ± 0.10	5	0.679 ± 0.003	−5.31 ± 0.02	−7.1 ± 0.3	9.5[c]
BU1-7	388–392	5.98 ± 0.05	5	0.678 ± 0.008	−5.32 ± 0.07	−7.1 ± 0.3	9.5[c]
BU1-8	502–504	7.0 ± 0.3*	6	0.681 ± 0.007	−6.16 ± 0.11	−7.4 ± 0.3	11.1[b]
BU1-9	565–570	7.5 ± 0.3*	5	0.693 ± 0.002	−5.76 ± 0.08	−6.7 ± 0.3	11.1[b]
BU1-10	~ 670	122 ± 3*	5	0.671 ± 0.007	−5.91 ± 0.02	−7.4 ± 0.3	11[d]
Stalagmite BU4							
BU4-1	0–0.5	0.03 ± 0.03	5	0.668 ± 0.007	−5.57 ± 0.14	−7.6 ± 0.3	9.5[e]
BU4-2	11–13.5	0.9 ± 0.3	5	0.677 ± 0.003	−5.07 ± 0.04	−7.0 ± 0.3	9.2[a]
BU4-3	20–28	1.1 ± 0.1	5	0.671 ± 0.003	−5.74 ± 0.06	−7.8 ± 0.3	9.2[a]
BU4-4	38–42	1.30 ± 0.05	6	0.669 ± 0.007	−6.14 ± 0.04	−8.2 ± 0.3	9.2[a]
BU4-5	42–45	1.30 ± 0.15	5	0.677 ± 0.006	−5.92 ± 0.07	−7.8 ± 0.3	9.2[a]
BU4-6	91–94	2.7 ± 0.1	5	0.667 ± 0.004	−5.73 ± 0.11	−7.8 ± 0.3	9.5[c]
BU4-7	94–96	2.9 ± 0.1	5	0.676 ± 0.004	−5.67 ± 0.05	−7.5 ± 0.3	9.5[c]
BU4-8	135–140	5.2 ± 0.1	5	0.692 ± 0.005	−6.05 ± 0.06	−7.6 ± 0.3	9.5[c]
BU4-9	210–214	8.2 ± 0.2	5	0.705 ± 0.005	−6.13 ± 0.05	−7.7 ± 0.3	8.5[c]
Stalagmite BU2							
BU2-1	50	10.3 ± 0.2	5	0.674 ± 0.007	−6.10 ± 0.07	−9.4 ± 0.3	5.1[b]
BU2-2	70	10.8 ± 0.2	5	0.669 ± 0.005	−6.04 ± 0.06	−9.5 ± 0.3	5.1[b]
BU2-3	225	53 ± 2*	6	0.702 ± 0.007	−5.42 ± 0.06	−8.6 ± 0.3	3.7[f]
BU2-4	250	53 ± 2*	5	0.696 ± 0.007	−5.58 ± 0.12	−8.9 ± 0.3	3.7[f]
Stalagmite BU-UWE							
BU-UWE-1	9–12	11.5 ± 0.4*	5	0.667 ± 0.005	−5.64 ± 0.09	−9.1 ± 0.3	5.1[b]
BU-UWE-2	22–26	11.6 ± 0.4*	6	0.663 ± 0.005	−5.80 ± 0.07	−9.3 ± 0.3	5.1[b]
BU-UWE-3	42–46	11.7 ± 0.4*	6	0.663 ± 0.004	−5.64 ± 0.05	−9.2 ± 0.3	5.1[b]
BU-UWE-4	56–63	53 ± 1*	5	0.692 ± 0.005	−4.70 ± 0.04	−8.1 ± 0.3	3.7[f]
BU-UWE-5	68–70	128 ± 3*	6	0.662 ± 0.008	−6.03 ± 0.05	−7.7 ± 0.3	11[d]
BU-UWE-6	72–75	129 ± 3*	5	0.668 ± 0.003	−5.62 ± 0.05	−7.2 ± 0.3	11[d]
BU-UWE-7	75–80	130 ± 3*	6	0.676 ± 0.011	−6.27 ± 0.18	−7.6 ± 0.4	11[d]

[a] Mann et al. (2008); [b] NGTs (Table 3); [c] Davis et al. (2003); [d] average of Guiot et al. (1989), Zagwijn (1996), Klotz et al. (2003), Felis et al. (2004) and Otto-Bliesner et al. (2006); [e] German Weather Service; [f] Guiot et al. (1989);

Table 3. Noble gas temperatures in stalagmites BU-UWE (Kluge et al., 2008) and BU1. The temperatures (NGT_{corr}) have been corrected using a constant offset by comparison with the multi-proxy temperature reconstruction of Mann et al. (2008). Noble gas concentrations and evaluation parameters are given in the Supplement. Mean 1 is the average value of BU1-B and BU1-C used for co-variation reconstruction of sample BU1-5, mean 2 is the average of BU1-DI to BU1-G II used for BU1-8 and BU1-9.

Sample	Distance from top (mm)	Age (kyr)	NGT_{corr} (°C)
BU1-A	50	0.6 ± 0.3	9.3 ± 0.9
BU1-B	220	4.7 ± 0.3	9.3 ± 1.2
BU1-C	290	4.9 ± 0.3	9.5 ± 1.5
Mean 1	220–290	–	9.4 ± 1.5
BU1-D I	460	6.8 ± 0.6	12.0 ± 5.6
BU1-D II	460	6.8 ± 0.6	11.7 ± 1.4
BU1-E	490	7.0 ± 0.5	10.1 ± 1.7
BU1-F	510	7.3 ± 0.2	11.2 ± 1.2
BU1-G I	550	7.5 ± 0.3	12.2 ± 2.3
BU1-G II	550	7.5 ± 0.3	9.7 ± 1.0
Mean 2	460–550	–	11.1 ± 1.0
BU-UWE			
Early Holocene		11–12	5.1 ± 0.9

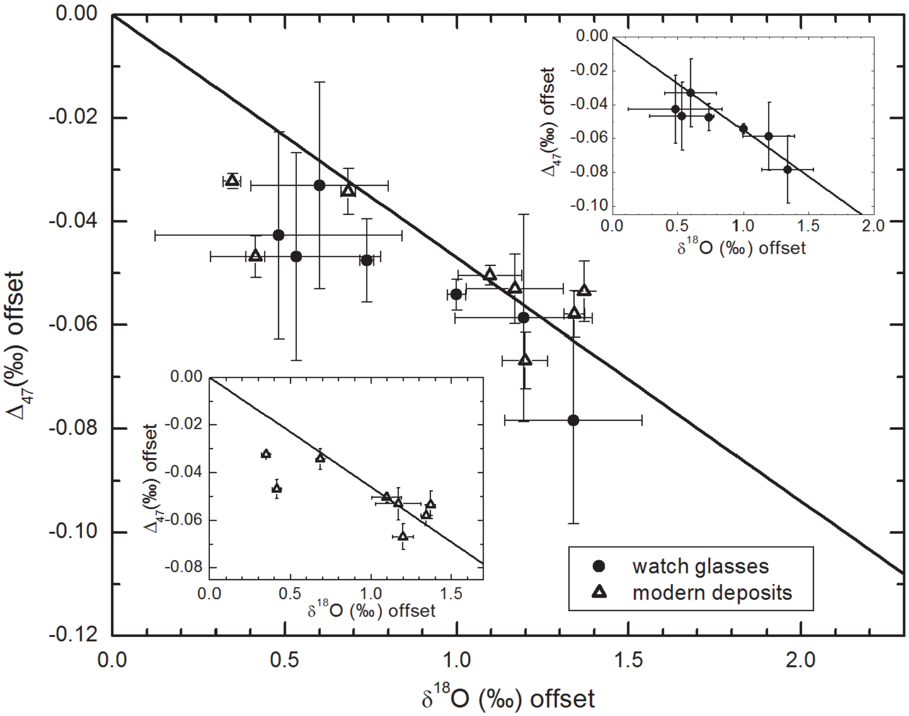

Fig. 1. Δ_{47} offset versus δ^{18}O offset in different sets of modern cave deposits. The thick line is a linear fit through all modern calcites. It reflects the variable degree of kinetic isotope fractionation and assumes that Δ_{47} and δ^{18}O vary together in both CO_2 degassing and hydration/hydroxylation reaction. The insets depict separate fits of calcite precipitates on watch glasses from Bunker Cave (upper inset) and modern calcites from adjacent caves (lower inset) resulting in similar slopes (watch glasses: −0.055, modern deposits excluding watch glasses: −0.046, all modern calcite precipitates: −0.047). The origin is defined as the expected equilibrium for both δ^{18}O and Δ_{47}.

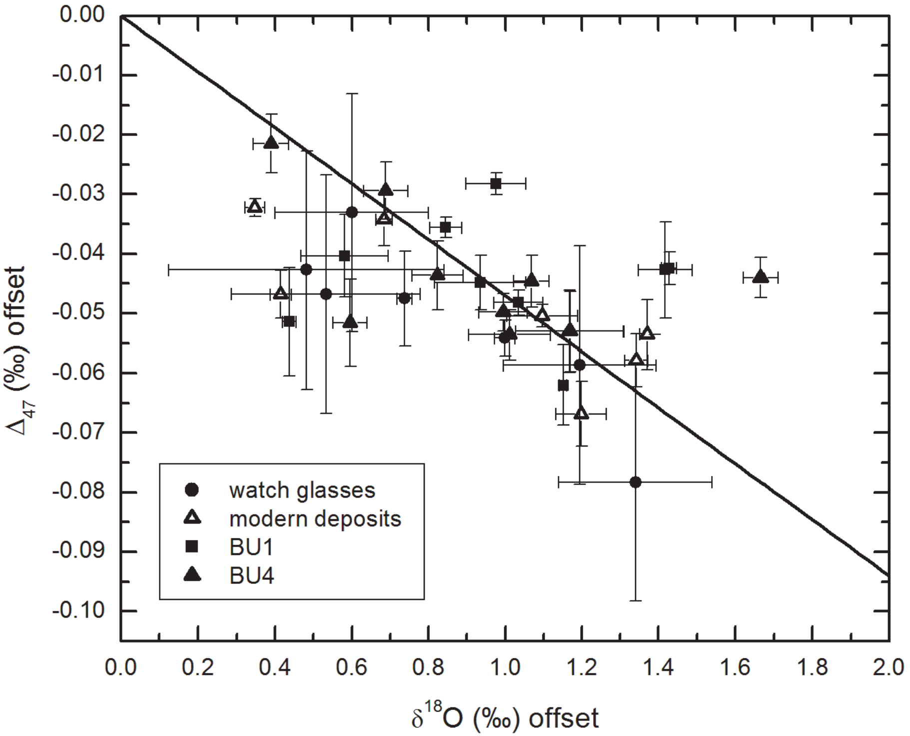

Fig. 2. Δ_{47} versus δ^{18}O offsets for Holocene stalagmites BU1 and BU4 as well as modern speleothems. The straight line is the slope obtained from a linear fit of modern calcite precipitates (Fig. 1).

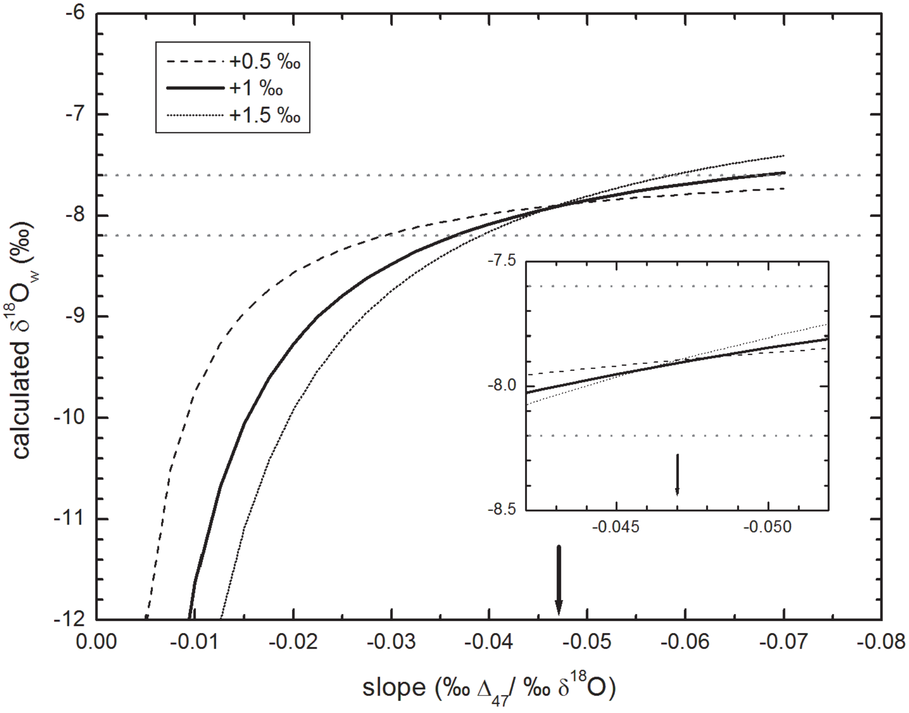

Fig. 3. Sensitivity analysis of the drip-water $\delta^{18}O_w$ values (calculated via the co-variation method) on the co-variation slope. The reference point is a slope of −0.047 (arrow on the bottom) and a drip-water value of −7.9 ‰, as observed for the modern deposits and the drip water of Bunker Cave. The dotted horizontal lines indicate a ±0.3 ‰ uncertainty range in the drip water around this reference value. The thick line refers to a sample that is 1 ‰ offset in calcite $\delta^{18}O_c$ from equilibrium. Lower (dashed line) and higher offsets (short dashed line) are also given for comparison. The inset shows the details around the reference slope value.

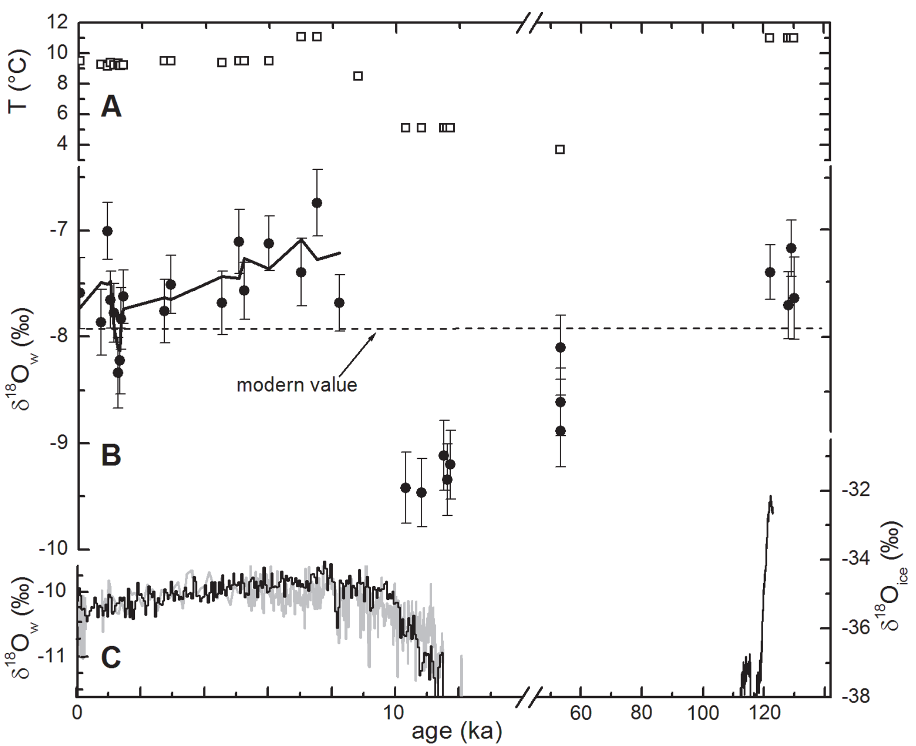

Fig. 4. Reconstructed drip-water $\delta^{18}O_w$ values of samples from stalagmites BU1, BU2, BU4 and BU-UWE **(B)** and the independent temperature estimates used **(A)**. The dashed line indicates the mean modern drip-water $\delta^{18}O_w$ value of −7.9 ‰; the thick black line is a threepoint smoothing of the Holocene data. Water $\delta^{18}O_w$ values from Lake Ammersee (**C**, left axis, three-point grey line; von Grafenstein et al., 1999) and ice-core $\delta^{18}O$ data from Greenland (**C**, right axis, black line; NGRIP members, 2004) are shown for comparison. Note the different scales on the y-axis and the break in the x-axis scale.

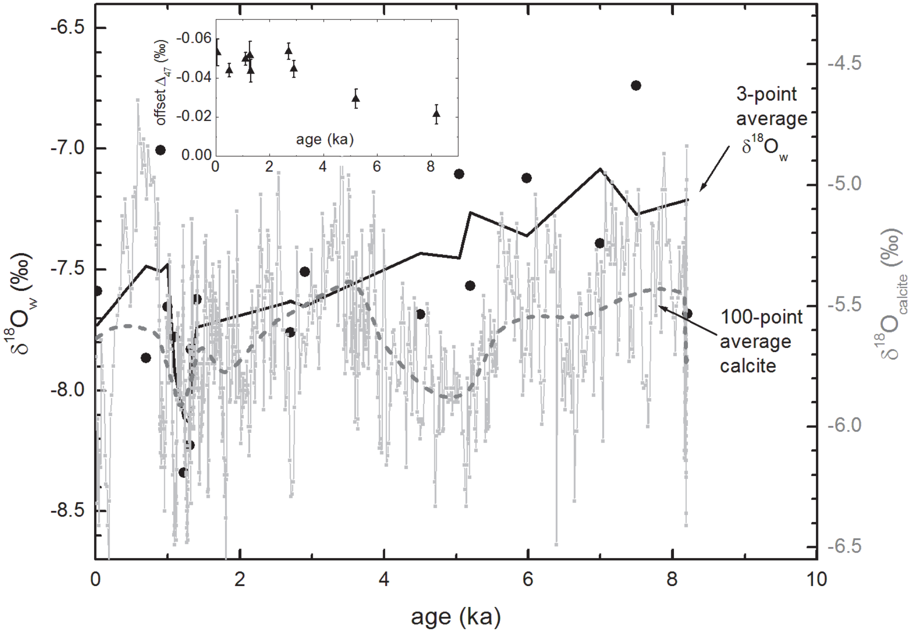

Fig. 5. Reconstructed drip-water $\delta^{18}O_w$ values based on the co-variation method (black circles, left axis) for stalagmites BU1 and BU4. The thick black line is a moving three-point average of the $\delta^{18}O_w$ values. The typical uncertainty of a single data point is 0.3 ‰. Calcite $\delta^{18}O_c$ values (grey, right axis) of stalagmite BU4 (adapted from Fohlmeister et al., 2012) and its 100-point moving average (dashed grey line) are given for comparison. The differences between both curves are attributed to changes in both temperature and kinetic isotope fractionation (given in the inset as the measured Δ_{47} offsets of stalagmite BU4).