

# Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by ‘clumped isotope’ thermometry

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## Abstract

‘Clumped isotope’ thermometry is based on analyzing mass 47 in CO<sub>2</sub> extracted from carbonates and uses the tracer mass 47 anomaly ( $\Delta_{47}$ ).  $\Delta_{47}$  is defined as the deviation of  $R^{47}$  from that expected for a random distribution of isotopologues and reflects a temperature dependent preference of <sup>13</sup>C and <sup>18</sup>O to create a bond with each other in CO<sub>2</sub> or in the carbonate lattice. Being an internal characteristic of the carbonate mineral, it is independent of the isotopic composition of the water in which equilibrium precipitation of the carbonate occurs and can therefore be used to independently determine carbonate growth temperatures. This work provides a first examination of the applicability of ‘clumped isotopes’ thermometry to reconstructing the growth temperatures of speleothems, by examining the glacial/interglacial variations of the  $\Delta_{47}$  values of speleothem carbonates from Soreq cave, Israel. The results indicate that the last glacial maximum temperatures were 6–7 °C colder than modern day temperature and a sample at 56 Ky BP was 3 °C colder than the modern. Early Holocene temperatures were slightly above modern day, and late Holocene temperatures were slightly below modern day. These temperature variations are similar to those previously estimated for Eastern Mediterranean sea surface water. Cave water was <sup>18</sup>O depleted in the Holocene compared to modern day (by 0.6–1‰) and 1.1‰ more enriched in the last glacial maximum. Comparison of these cave water  $\delta^{18}\text{O}$  values with fluid inclusion  $\delta D$  values indicated a late Holocene d-excess value within the range of modern rainfall, implying ~45% relative humidity. Last glacial maximum and early Holocene d-excess values were significantly lower, suggesting relative humidity of ~60% and ~70%, respectively. The temperatures reported in this study were empirically corrected for a non-equilibrium artifact observed in a modern speleothem. The similarity of the temperature variations obtained here to other, independent, records in the region suggests that the  $\Delta_{47}$ –temperature calibration slope observed in inorganic synthetic calcite and marine organisms may also be applied in speleothems. But the offset observed in modern temperature suggests that the intercept is different so that a separate calibration is needed for accurate absolute temperature reconstruction using speleothem ‘clumped isotopes’. Similar examination of additional caves would be necessary to determine whether such empirical correction can be generally applied or is it a unique characteristic of Soreq cave.

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## 1. INTRODUCTION

The oxygen isotopic composition of carbonate minerals is widely used as a proxy for climatic variations. Its use is based on the temperature dependency of the isotope exchange equilibrium between the carbonate mineral and the water from which it precipitates (e.g., McCrea, 1950;

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Epstein et al., 1953; Emiliani, 1966; O'Neil et al., 1969; Kim and O'Neil, 1997). Carbonate cave deposits provide an excellent source material for efforts to reconstruct past climatic conditions on land. Cave bedrock temperatures normally reflect annual mean surface temperatures (e.g., Poulson and White, 1969; McDermott et al., 2005), making speleothems a useful, well-dated, archive material, whose  $\delta^{18}\text{O}$  values can provide high-resolution continental climatic records (for reviews see Schwarcz, 1986; Gascoyne, 1992; McDermott, 2004; McDermott et al., 2005). However, the use of carbonate  $\delta^{18}\text{O}$  for deducing paleoclimatic conditions suffers a disadvantage in that its value reflects a combination of variations in temperatures and isotopic composition of the parent solution. This is a particular problem in continental records, owing to the complex nature of  $\delta^{18}\text{O}$  variations in rainwater.

Carbonate 'clumped isotopes' thermometry is based on abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in the carbonate lattice. It can be used to determine carbonate growth temperatures, independent of the oxygen isotopic composition of the solution from which the carbonate precipitates (Ghosh et al., 2006a). As such, it can be used in conjunction with the  $\delta^{18}\text{O}$  values of the carbonate to constrain the  $\delta^{18}\text{O}$  values of past precipitation. 'Clumped isotope' thermometry is based on the mass spectrometric analysis of mass 47 in  $\text{CO}_2$  extracted by phosphoric acid digestion of carbonates. It is reported using the  $\Delta_{47}$  value, which is defined as the deviation of the isotopic ratio  $R^{47}$  from that at a random distribution of isotopologues, and is therefore a measure for the temperature dependent thermodynamic preference for two heavy isotopes to create a chemical bond with each other. At thermodynamic equilibrium, C–O bonds in carbonates (and, therefore, in the  $\text{CO}_2$  extracted from carbonates) approach the random isotopologue distribution ( $\Delta_{47} = 0$ ) at high temperatures, but preferentially 'clump'  $^{13}\text{C}$  and  $^{18}\text{O}$  into bonds with each other to produce positive  $\Delta_{47}$  values as temperatures decrease. Kinetic isotope effects have been recognized (Guo et al., 2007; Guo, 2008), and can potentially modify this equilibrium signature in some cases.

Calibration of  $\Delta_{47}$  vs. temperature was performed using calcite precipitated inorganically at known temperatures (Ghosh et al., 2006a) by a modification of the method first described by McCrea (1950). This approach was successfully applied to temperature determination in paleosol nodules (Ghosh et al., 2006b), brachiopods, mollusks (Came et al., 2007) and carbonates from meteorites (Guo and Eiler, 2007). In this work, we apply this approach to speleothems from the Soreq cave, in Israel, where a detailed  $\delta^{18}\text{O}$  record exists covering the last 185 Ky (Bar-Matthews et al., 2000; Ayalon et al., 2002). We focus on the last glacial–interglacial transition, examining  $\Delta_{47}$  values and their application to cave temperature determination, during the early and late Holocene, last glacial maximum (LGM), and a sample earlier in the last glacial period. We then use the temperatures obtained to estimate  $\delta^{18}\text{O}$  values of cave water that, together with previously determined  $\delta D$  values of fluid inclusions (McGarry et al., 2004), provide constraints on variations in rainfall in the region. Comparing these data to existing, independent, temperature estimates in the cave and the region provides a feasibility test for

the applicability of 'clumped isotopes' thermometry to speleothem material.

## 2. METHODOLOGY

Speleothem samples were pieces from the side of Soreq cave laminae (not along the growth axis) that were previously dated and analyzed for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (Bar-Matthews et al., 1997; Bar-Matthews et al., 1999; Bar-Matthews et al., 2000; Bar-Matthews et al., 2003) and later used for  $\delta D$  analyses of fluid inclusions (McGarry et al., 2004). The samples analyzed are grouped as late Holocene (2-6 and 2-6-A, dated 0.9–1.9 and 0.9 Ky BP, respectively), early Holocene (2-8-E, dated 8–10 Ky BP, 2-20(1–5), dated 7.2–8.8 Ky BP, 2-20-7, dated 8.7 Ky BP), last glacial maximum (7-23-A, dated 19–19.4 Ky BP, 12-Z-B, dated 19–20 Ky BP) and earlier during the last glacial (9-25-G, dated 56 Ky BP). In order to calibrate the  $\Delta_{47}$  system for speleothems, a modern speleothem (labeled 12-1-57), deposited during the last 30 years on the path that was constructed in 1976 before the cave was opened to the public, was analyzed.

Samples 2-6-A, 2-20-7, 7-23-A and 12-Z-B were ground using an agate mortar and pestle. Aliquots were taken from each of the other samples and ground similarly. No cleaning treatment was applied to the carbonate samples. Powdered carbonate ( $\sim 10$  mg) was digested overnight by phosphoric acid at 25 °C (as described by Ghosh et al., 2006a) in order to extract  $\text{CO}_2$  for mass spectrometric analysis. Each sample was analyzed in 2–6 replicates of  $\text{CO}_2$  extraction (Table 1). This level of replication is required to obtain the desired precision.

$\text{CO}_2$  was purified of potential contaminants, such as hydrocarbons, by a dry ice–ethanol slush as well as by passing it through a GC column (Supleco Q plot, 530  $\mu\text{m}$  ID, 30 m long) at  $-20$  °C, with column baking at 150 °C between samples (Affek and Eiler, 2006; Ghosh et al., 2006a).  $\text{CO}_2$  was analyzed by dual inlet mass spectrometry using a Finnigan MAT-253 gas source isotope ratio mass spectrometer that was configured for measurements of masses 44–49, to obtain  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\Delta_{47}$  values, with masses 48 and 49 being used to detect residual hydrocarbon contamination. A detailed description is given in Eiler and Schauble (2004). Measurements of each  $\text{CO}_2$  sample gas consisted of 5–9 analyses, each of which involves 10 cycles of sample-standard comparison with an ion integration time of 8 s per cycle.

$\Delta_{47}$  is calculated from the measured ratios ( $R^i$ ) of masses 45, 46 and 47 to mass 44 as:

$$\Delta_{47} = \left[ \frac{R^{47}}{2R^{13} \cdot R^{18} + 2R^{17} \cdot R^{18} + R^{13} \cdot (R^{17})^2} - \frac{R^{46}}{2R^{18} + 2R^{13} \cdot R^{17} + (R^{17})^2} - \frac{R^{45}}{R^{13} + 2R^{17} + 1} + 1 \right] \times 1000 \quad (1)$$

and the  $\Delta_{47}$  calibration is obtained by measuring  $\text{CO}_2$  heated to 1000 °C, which is assumed to have a random distribution of isotopes among all isotopologues (Eiler and Schauble, 2004; a detailed description of the method is given in Affek and Eiler, 2006). There is no accepted standard

Table 1  
Observed isotopic composition in the measured speleothem samples

Sample	Age <sup>a</sup> (Ky)	<i>n</i> <sup>b</sup>	δ <sup>13</sup> C <sup>c</sup> (‰)	δ <sup>18</sup> O <sup>b</sup> (‰)	Δ <sub>47</sub> (‰)	δ <i>D</i> <sup>a</sup> (‰)
12-1-57	0.03	6	-9.53 ± 0.01	-5.25 ± 0.004	0.642 ± 0.003	
2-6-A	0.9	5	-11.09 ± 0.004	-5.58 ± 0.01	0.641 ± 0.005	-6 ± 6.5 <sup>d</sup>
2-6	0.9–1.9	6	-10.80 ± 0.01	-5.47 ± 0.01	0.660 ± 0.005	
2-20 (1–5)	7.2–8.8	4	-7.05 ± 0.26	-6.42 ± 0.02	0.647 ± 0.001	
2-20-7	8.7	2	-5.17 ± 0.01	-6.59 ± 0.03	0.628 ± 0.008	
2-8-E	8–10	5	-7.49 ± 0.29	-6.25 ± 0.03	0.641 ± 0.002	-31.6 ± 1.6
7-23-A	19–19.4	2	-7.86 ± 0.04	-2.67 ± 0.01	0.673 ± 0.006	-16 ± 3.3
12-Z-B	19–20	3	-8.64 ± 0.004	-3.00 ± 0.02	0.668 ± 0.002	-11.4 ± 5.0
9-25-G	56	3	-10.44 ± 0.02	-4.29 ± 0.004	0.657 ± 0.006	-15.4 ± 5.0

Samples are labeled as in McGarry et al. (2004).

<sup>a</sup> Data from McGarry et al. (2004).

<sup>b</sup> *n* reflects the number of CO<sub>2</sub> extraction replicates, with 50–90 sample-standard mass spectrometer comparisons per extraction.

<sup>c</sup> Both δ<sup>13</sup>C and δ<sup>18</sup>O are given in VPDB scale. δ*D* is given in the VSMOW scale.

<sup>d</sup> Fluid inclusion δ*D* for the late Holocene samples was analyzed using the outer layer of the 2–6 speleothem and probably included a longer time span than that of 2-6-A but shorter than 2–6.

material, which is known to be homogenous in its Δ<sub>47</sub> values and whose Δ<sub>47</sub> value is known. The closest to it are the measurements of CO<sub>2</sub> extracted by acid digestion of the marble standard NBS-19 (Δ<sub>47</sub> = 0.352‰; Ghosh et al., 2006a) as well as measurements of a cylinder CO<sub>2</sub> (δ<sup>13</sup>C = -10.7‰, δ<sup>18</sup>O = 31.9‰, Δ<sub>47</sub> = 0.871‰; Affek et al., 2007), whose Δ<sub>47</sub> values were previously determined in numerous analyses over a long time period. The precision of this method can be estimated using repeated measurements of both these materials, over the time period in which the speleothem samples were measured, to be about 0.005‰ (1 standard error, *n* = 10 replicates of CO<sub>2</sub> extraction from NBS-19 and *n* = 23 aliquots of cylinder CO<sub>2</sub>), which is equivalent to ±1 °C at the temperature range around ambient. This is also the mean SE obtained for the speleothem samples when considering the number of replicates of CO<sub>2</sub> extraction given in Table 1 (between 2 and 6) and between 50 and 90 sample-standard comparisons in the mass spectrometer measurement for each CO<sub>2</sub> extraction. This precision is consistent with measurements being close to the 'shot-noise' limit (Merritt and Hayes, 1994).

Samples were measured in three batches over the course of 9 months. This could result in potential variations due to systematic errors in sample preparation that vary over time. The two working standards described above, measured with the samples, were used to correct for this. These materials were selected as standards since their Δ<sub>47</sub> values have been accurately characterized by numerous measurements made over a prolonged time period prior to this study, and because their Δ<sub>47</sub>, δ<sup>18</sup>O and δ<sup>13</sup>C values bracket the values observed in the speleothem samples. The correction varied between 0.024 and 0.037‰ for the first batch of samples but was close to zero (average of -0.001 and 0.002‰, respectively) in the other batches and resulted in reduced variance for samples analyzed in more than one batch.

Temperature information is derived using the Δ<sub>47</sub> calibration of Ghosh et al. (2006a) obtained from isotopic measurements of synthetic calcite precipitated inorganically at known temperatures by degassing of CO<sub>2</sub> from saturated calcium bicarbonate bulk solutions. This yielded a Δ<sub>47</sub>-temperature relationship of Δ<sub>47</sub> = 0.0592 × 10<sup>6</sup>/T<sup>2</sup> - 0.02

(where *T* is the absolute temperature). This calibration was further tested using Δ<sub>47</sub> measurements of natural carbonates, mostly from marine organisms, grown at known temperatures. These measurements mostly agree with the original inorganic calibration (Ghosh et al., 2006a; Came et al., 2007; Eiler and Tripathi, 2007; Tripathi et al., 2007). However, despite the large number of carbonate materials that appear to conform to this nominally equilibrium calibration, kinetic isotope effects that can disturb this equilibrium have been recognized in carbonates grown by vigorous degassing of CO<sub>2</sub> from aqueous solutions (Guo et al., 2007; Guo, 2008). Speleothems commonly grow from thin films that are super-saturated in CO<sub>2</sub>, conditions in which CO<sub>2</sub> degassing is the rate determining step for carbonate growth (Buhmann and Dreybrodt, 1985; Dreybrodt, 1999). Thus, speleothem formation is potentially more susceptible to kinetic isotope effects like those described by Guo (2008) as compared to carbonates precipitation in bulk solution. We used a modern speleothem (12-1-57) in order to assess the importance of such effects in speleothem 'clumped isotopes' thermometry.

Having obtained the temperature of carbonate precipitation based on the Δ<sub>47</sub> value of extracted CO<sub>2</sub>, the observed δ<sup>18</sup>O values of the carbonate can then be used to calculate the δ<sup>18</sup>O values of the water (δ<sup>18</sup>O<sub>water</sub>) from which the calcite was precipitated. δ<sup>18</sup>O of the calcite (δ<sup>18</sup>O<sub>calcite</sub>) is calculated from the values of the extracted CO<sub>2</sub> assuming a fractionation factor of α<sub>CaCO<sub>3</sub>-CO<sub>2</sub>(acid)</sub> = 10.25‰ in the phosphoric acid digestion reaction at 25 °C (Sharma and Clayton, 1965; Kim et al., 2007). δ<sup>18</sup>O values of the water in equilibrium with this calcite are calculated using the equation of Kim and O'Neil (1997) modified to fit the above α<sub>CaCO<sub>3</sub>-CO<sub>2</sub>(acid)</sub> value. The original Kim and O'Neil (1997) α<sub>calcite-H<sub>2</sub>O</sub> temperature dependence was obtained using a value of 10.44‰ for α<sub>CaCO<sub>3</sub>-CO<sub>2</sub>(acid)</sub>. This value was recently corrected to 10.25‰ (Kim et al., 2007) requiring a corresponding modification for α<sub>calcite-H<sub>2</sub>O</sub>. We use the modification given by Bohm et al. (2000): 1000 ln α<sub>calcite-H<sub>2</sub>O</sub> = 18.03 × 10<sup>3</sup>/T - 32.17, with *T* in Kelvin. Note that δ<sup>18</sup>O<sub>calcite</sub> values used in this calibration are given in the SMOW scale. However, speleothem

carbonate  $\delta^{18}\text{O}$  values are normally reported in the PDB scale. The  $\delta^{18}\text{O}_{\text{carbonate}}$  results given in this work are reported as PDB values and converted to SMOW for the fractionation calculation using the relationship defined in Friedman and O'Neil (1977) and Gonfiantini et al. (1993).

### 3. RESULTS

The values of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\Delta_{47}$  for speleothem carbonate from Soreq cave are given in Table 1. Although the material analyzed in this work was obtained from the side of the laminae instead of the central growth axis (to allow for the relatively large amount of material needed for  $\Delta_{47}$  analysis), the measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values reflect the trends found previously for the Soreq cave (e.g., Bar-Matthews et al., 2000).  $\delta^{13}\text{C}$  values are relatively  $^{13}\text{C}$ -depleted ( $-10.9\text{‰}$ ) in the Late Holocene samples (1–2 Ky BP) and the 56 Ky BP sample ( $-10.4\text{‰}$ ), more enriched ( $-8.3\text{‰}$ ) during the last glacial maximum (LGM, 19–20 Ky BP) and even more enriched ( $-6.6\text{‰}$ ) in the early Holocene samples (7–10 Ky BP).  $\delta^{18}\text{O}$  values are relatively high in the LGM samples ( $-2.8\text{‰}$ ), lower in the 56 Ky BP sample ( $-4.3\text{‰}$ ) and still lower in the Holocene ( $-6.1\text{‰}$ ) samples, especially during the early Holocene ( $-6.4\text{‰}$ ), when Sapropel layers appear in Eastern Mediterranean sediments (Bar-Matthews et al., 2000).

The observed  $\Delta_{47}$  values of LGM speleothem samples are  $0.673\text{‰}$  and  $0.668\text{‰}$  for samples dated 19 and 19–20 Ky, respectively. Late Holocene samples have values of  $0.641\text{‰}$  and  $0.660\text{‰}$ .  $\Delta_{47}$  values in early Holocene samples vary between  $0.628\text{‰}$  and  $0.647\text{‰}$ . The 56 Ky BP sample gives a  $\Delta_{47}$  value of  $0.657\text{‰}$ . The sample of a modern speleothem analyzed for the purpose of calibrating the 'clumped isotope' system for speleothems gave a  $\Delta_{47}$  value of  $0.642\text{‰}$ . Error estimates are given in Table 1.

### 4. DISCUSSION

#### 4.1. Calibration of the $\Delta_{47}$ temperatures using modern day speleothem

As originally noted by Bar-Matthews et al. (1996), it is necessary to examine the stable isotope system in a cave using present-day speleothem material as guide to the deposition characteristics. When we apply the nominally equilibrium inorganic calibration of the  $\Delta_{47}$  thermometer of Ghosh et al. (2006a) to data for the modern speleothem from Soreq cave, we obtain an apparent growth temperature of  $26\text{ °C}$  (Table 1). This value is significantly higher than the cave temperature over the growth period. The mean annual temperature of the bedrock above the cave is estimated to be  $18\text{ °C}$  (Ayalon et al., 1998). However, the air temperature within the cave has increased to  $22\text{--}23\text{ °C}$  in the last 30 years since the cave was opened to public tours and lighting was added. The modern speleothem sample analyzed here was deposited on the path that was constructed when the cave was opened, indicating that it is not more than 30 years old. This speleothem was formed under a fast water drip, which is mainly active in the winter

rainy season. The fast drips typically reflect thermal equilibrium with the bedrock, not having sufficient time to re-equilibrate to the cave air temperature (Ayalon et al., 1998). We therefore suspect that the speleothem grew at the  $18\text{--}19\text{ °C}$  temperature of the bedrock. This is confirmed by the  $\delta^{18}\text{O}$  value of this sample ( $-5.25\text{‰}$ ) that, as is the case for most modern speleothems in the cave, overlaps with the values expected for approximate equilibrium at  $\sim 18\text{ °C}$  with waters that are within the range of observed cave water ( $-3.5\text{‰}$  to  $-6.3\text{‰}$ ; Bar-Matthews et al., 1996).

Thus, the apparent temperature recorded by clumped isotope thermometry for the modern speleothem sample is  $\sim 8\text{ °C}$  too high. It is not likely to be the result of contamination or re-equilibration during sample preparation, because both types of sample compromise would result in higher than expected  $\Delta_{47}$  values, opposite of the observation. This direction of offset is consistent with a recently-discovered kinetic isotope effect that occurs during rapid degassing of  $\text{CO}_2$  from calcite-saturated aqueous solutions (Hendy, 1971; Guo, 2008). This effect occurs because dissociation of  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$  (DIC) preferentially breaks  $^{12}\text{C}\text{--}^{16}\text{O}$ ,  $^{13}\text{C}\text{--}^{16}\text{O}$  and  $^{12}\text{C}\text{--}^{18}\text{O}$  bonds faster than it does  $^{13}\text{C}\text{--}^{18}\text{O}$  bonds, and thus the product  $\text{CO}_2$  is higher in  $\Delta_{47}$  than the bicarbonate ions from which it evolved. This also affects the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of the calcite, and leads to the well-known enrichment in  $\delta^{13}\text{C}$  along a stalagmite lamina (Fantidis and Ehhalt, 1970; Hendy, 1971). When degassing and precipitation are slow enough, the DIC can undergo a full oxygen isotope exchange with water, thus erasing the kinetic enrichment in  $^{18}\text{O}$  and leading to equilibrium values in both  $\delta^{18}\text{O}$  and  $\Delta_{47}$ . If, however, degassing is rapid compared to the rate of isotopic exchange between DIC and water, this will leave a relative deficit of  $^{13}\text{C}\text{--}^{18}\text{O}$  bonds in residual DIC species, and thus lower than equilibrium  $\Delta_{47}$  values and higher than equilibrium apparent temperatures in carbonates grown from that DIC (Guo et al., 2007; Guo, 2008). Since the extent of exchange between DIC and water that is required for full equilibrium is similar in  $\Delta_{47}$  and  $\delta^{18}\text{O}$  (approximately 15 hydration–dehydration steps for full equilibrium, in analogy to the  $\delta^{18}\text{O}$  discussion in Gillon and Yakir (2000)) then offset from equilibrium should progress simultaneously in both tracers.

We can therefore assess the relevance of this effect by considering that the range of  $\delta^{18}\text{O}$  values observed for the water of the individual drip that feeds our modern speleothem is  $-5.32 \pm 0.76\text{‰}$  (for drip water collected between 1993 and 2000; the data till 1997 is given in Bar-Matthews et al., 1996; Ayalon et al., 1998), and using the kinetic isotope effect covariance of  $\delta^{18}\text{O}$  and  $\Delta_{47}$ , as developed by Guo (2008). This can be illustrated by considering that at equilibrium, since both tracers vary with temperature, there is a correlation between  $\Delta_{47}$  and  $\delta^{18}\text{O}_{\text{calcite}}$ , assuming a constant  $\delta^{18}\text{O}$  value of drip water (using  $-5.32\text{‰}$  for our drip water and the temperature dependency given above, yields a correlation of  $\Delta_{47} = 0.000194(\delta^{18}\text{O}_{\text{calcite}})^2 + 0.0257\delta^{18}\text{O}_{\text{calcite}} + 0.832$ ). For a temperature of  $18\text{ °C}$  calcite in equilibrium with the mean drip water ( $-5.32\text{‰}$ ) should have  $\delta^{18}\text{O}$  value of  $-6.27\text{‰}$ , significantly offset from the observed value of  $-5.25\text{‰}$ . Kinetic isotope effect would then cause a deviation from this correlation, that at any

given temperature would follow a KIE  $\Delta_{47}/\delta^{18}\text{O}$  trajectory slope (Guo, 2008). For 18 °C with an estimated KIE  $\Delta_{47}/\delta^{18}\text{O}$  slope of  $-0.024$ , the  $\delta^{18}\text{O}$  associated with  $\Delta_{47}$  of  $0.642\text{‰}$  would be  $-4.75 \pm 0.74\text{‰}$ , within error from the observed value of  $-5.25\text{‰}$  (the estimated error is the result of the variability observed in  $\delta^{18}\text{O}$  of the particular drip water). The observed combination of  $\Delta_{47}$  and  $\delta^{18}\text{O}$  is consistent with the kinetic effect that would be expected at  $\sim 19\text{ °C}$ , consistent with the modern day cave temperature being slightly higher than the bedrock temperature (see above).

In principle, we should be able to demonstrate the role of kinetic isotope effects in our analyzed speleothems using the Hendy test (Hendy, 1971). Concurrent enrichment along a lamina of both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  is considered to reflect precipitation under non-equilibrium conditions, whereas enrichment of  $\delta^{13}\text{C}$  at constant  $\delta^{18}\text{O}$  should occur when speleothem is precipitated at equilibrium. Similarly, under non-equilibrium conditions,  $\Delta_{47}$  values are expected to decrease and be negatively correlated with  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (Guo et al., 2007; Guo, 2008) whereas, constant  $\Delta_{47}$  values across a lamina would be expected when calcite is precipitated at equilibrium. Previous applications of the Hendy test to Soreq cave samples showed no correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , suggesting equilibrium deposition (Bar-Matthews et al., 1993; Bar-Matthews et al., 1996). The result of this test for two of the laminae analyzed here is given in Table 2. Similar variations were observed for other laminae of the same stalagmites, suggesting that precipitation conditions in Soreq cave are close to equilibrium. As part of the current work, we could not perform a strict Hendy test, as only a relatively small piece of each lamina

was available for analysis. We therefore performed a test for inhomogeneity for samples 12-1-57 and 2-8-E by analyzing powders collected from several sub-samples at different location along the lamina part available. This was done at a  $\sim 2\text{ cm}$  distance between sub-samples for 2-8-E and  $\sim 0.5\text{ cm}$  distance for 12-1-57. Relatively large variations were observed in  $\delta^{13}\text{C}$  in these samples, but  $\delta^{18}\text{O}$  and  $\Delta_{47}$  values were homogenous (Table 2), also implying that the samples were precipitated under close to equilibrium conditions.

However, the Hendy test might not be sufficiently sensitive to detect the modest kinetic isotope effects that would be required to explain our data for the modern speleothem. The  $\delta^{18}\text{O}$  offset between observed and equilibrium values is  $\sim 1\text{‰}$ . Such kinetic isotope effect could result from about 10% loss of DIC from  $\text{CO}_2$  degassing (based on Fig. 6 in Mickler et al., 2004)—an amount that is typically considered negligible (Mickler et al., 2004) and is lost within the natural variability observed in cave drip water.  $\Delta_{47}$  seem to be especially sensitive to dis-equilibrium. One reason for it might be simply the association of  $\Delta_{47}$  with cave temperature, which is much less variable than  $\delta^{18}\text{O}$  of cave water, so that dis-equilibrium is more apparent in  $\Delta_{47}$  than in  $\delta^{18}\text{O}$ .

We therefore hypothesize that the lower-than-equilibrium  $\Delta_{47}$  value of the modern speleothem is due to a kinetic isotope effect caused by  $\text{CO}_2$  degassing, in amounts too small to generate noticeable correlations between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Furthermore, we suggest that this effect is characteristic of speleothem precipitation, and so constitutes a common, material-specific isotope effect. Kinetic isotope effect is typically not very sensitive to temperature.

Table 2  
Results of Hendy and inhomogeneity tests, indicating that the speleothems were deposited close to isotopic equilibrium

Sub-sample	$\delta^{13}\text{C}(\text{‰})^a$	$\delta^{18}\text{O}(\text{‰})^a$	Sub-sample	$\delta^{13}\text{C}(\text{‰})^a$	$\delta^{18}\text{O}(\text{‰})^a$	$\Delta_{47}(\text{‰})$
<i>2-6-A</i>			<i>2-8-E<sup>b</sup></i>			
5	-11.08	-4.24	A	-7.05	-6.35	0.639
10	-12.8	-6.19	A	-7.01	-6.08	0.649
15	-10.44	-5.21	A	-7.05	-6.33	0.630
20	-11.68	-5.75	B	-6.30	-6.34	0.649
25	-11.25	-5.7	C	-10.04	-6.11	0.641
30	-10.41	-6.12				
Average	-11.29	-5.54	Average	-7.49	-6.23	0.641
Std. dev.	0.89	0.73	Std. dev. <sup>c</sup>	1.98	0.12	0.005
<i>12-Z-B</i>			<i>12-1-57<sup>b</sup></i>			
15	-7.05	-2.41	A	-9.38	-5.15	0.642
20	-7.33	-2.31	A	-9.36	-5.21	0.649
25	-7.48	-2.39	A	-9.36	-5.21	0.638
30	-7.89	-2.11	A	-9.32	-5.41	0.666
35	-8.78	-2.71	B	-9.86	-5.24	0.618
40	-8.42	-2.29	C	-9.89	-5.27	0.640
Average	-7.82	-2.37	Average	-9.53	-5.25	0.642
Std. dev.	0.67	0.20	Std. dev. <sup>c</sup>	0.30	0.012	0.016

<sup>a</sup> Both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are given in VPDB scale.

<sup>b</sup> Sub-samples are taken at the distance of  $\sim 2\text{ cm}$  from each other for 2-8-E and  $\sim 0.5\text{ cm}$  for 12-1-57. For samples 2-6-A and 12-Z-B the sub sample numbers indicate the distance from the bottom of the stalagmite (cm).

<sup>c</sup> Standard deviation for samples 2-8-E and 12-1-57 is calculated from the variations between the average of sub-samples A and sub-samples B and C.

However, the observed dis-equilibrium may vary with other climate sensitive precipitation parameters, such as rate of degassing and precipitation. At this stage it is impossible to predict how and to what extent would  $\Delta_{47}$  vary with such factors and the effect of precipitation conditions will have to be further studied prior to wide application of  $\Delta_{47}$  thermometry in speleothem.

As a first approximation, though, the dis-equilibrium offset can be corrected for empirically by using the observed modern sample offset. We do that by subtracting 8 °C (the difference between observed and actual growth temperatures for the modern sample) from measured apparent temperatures in all other samples. Below we will test the robustness of this proposed 8 °C correction by comparing the resulting record of temperature change and  $\delta^{18}\text{O}_{\text{water}}$  in Soreq cave to multiple, independent constraints.

Finally, it should be noted, that this correction for the isotope effects associated with  $\text{CO}_2$  degassing from thin films is important only for  $\Delta_{47}$ ; the required correction implies changes in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  that are small compared to natural variations and would not invalidate previous suggestions that Soreq cave carbonates grow at or near equilibrium (Bar-Matthews et al., 1993, 1996).

#### 4.2. Isotopic temperatures

The temperatures obtained from the  $\Delta_{47}$  measurements, both assuming the equilibrium calibration and adopting our suggested correction based on the modern speleothem data, are given in Table 3 and Fig. 1. We focus our discussion on the ‘corrected’ values, as we think they best represent growth temperatures. The resulting glacial temperatures are 11–12 °C for the LGM samples and 15 °C at 56 Ky BP. Late Holocene samples resulted in temperatures of 14 and 18 °C, slightly lower than modern day mean annual temperatures. Early Holocene samples resulted in temperatures between 17 and 21 °C, similar to or above modern day temperatures.

D/H values of fluid inclusions were previously analyzed in several of the samples studied in this work; these data were previously combined with the  $\delta^{18}\text{O}$  values of the spe-

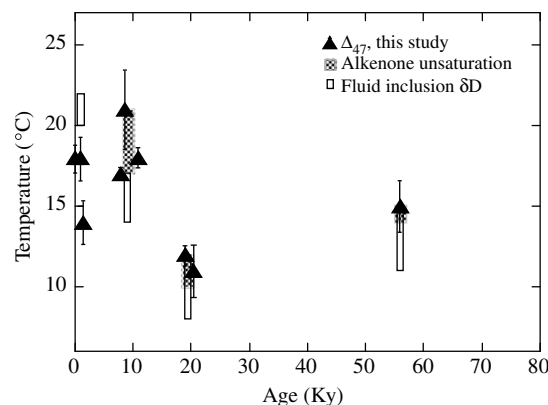


Fig. 1. Comparison of the temperatures obtained in this study using ‘clumped isotopes’ thermometry ( $\Delta_{47}$ , full triangles. Temperatures are corrected to a kinetic isotope effect of 8 °C; see text) to independent temperature estimates in the Eastern Mediterranean, using alkenone unsaturation levels (full gray bars; Emeis et al., 2003) and in Soreq cave using fluid inclusion  $\delta D$  (empty black bars; McGarry et al., 2004).

leothem carbonate to calculate the  $\delta^{18}\text{O}$  of the water and to estimate carbonate growth temperatures (McGarry et al., 2004). The ‘corrected’  $\Delta_{47}$  temperatures obtained here are consistent with these previous, independent estimates (Table 3 and Fig. 1). Note that our results are generally at the upper end of the range of these previous estimates. For the early Holocene samples this is probably because the fluid inclusion temperature estimate assumes that the d-excess in an interglacial must be within the modern day range, whereas the ‘clumped isotopes’ temperature implies that it might have been closer to the global meteoric water line (see below). For the rest of the samples, taking into consideration the analytical error in  $\delta D$  measurement, the d-excess values estimated using the ‘clumped isotopes’ temperatures are well within the range of the d-excess estimates in McGarry et al. (2004; see Table 1), suggesting no real difference between the two temperature estimates.

Table 3

Temperatures deduced from  $\Delta_{47}^a$  and from fluid inclusion  $\delta D$ ,  $\delta^{18}\text{O}$  of cave water deduced from the  $\Delta_{47}$  temperatures, and d-excess in these cave water<sup>b</sup>

	Sample	Age (Ky)	$\Delta_{47}$ temp. (°C)	Corrected temp. <sup>a</sup> (°C)	Fluid inclusion temp. (°C)	$\delta^{18}\text{O}_{\text{water}}$ (‰)	d-excess (‰) <sup>b</sup>
Modern	12-1-57	0.03	26 ± 1	18		-4.27 ± 0.14	
Late Holocene	2-6-A	0.9	26 ± 1	18	20–22	-4.52 ± 0.24	30.1
Late Holocene	2-6	0.9–1.9	22 ± 1	14		-5.31 ± 0.24	
Early Holocene	2-20(1-5)	7.2–8.8	25 ± 0.2	17		-5.70 ± 0.05	
Early Holocene	2-20-7	8.7	29 ± 2	21		-4.96 ± 0.39	
Early Holocene	2-8-E	8–10	26 ± 1	18	14–17	-5.26 ± 0.10	10.5
LGM	7-23-A	19–19.4	19 ± 1	11	8–11	-3.07 ± 0.28	8.5
LGM	12-Z-B	19–20	20 ± 0.4	12	9–12	-3.23 ± 0.09	14.4
LG	9-25-G	56	23 ± 1	15	11–15	-4.01 ± 0.28	16.7

<sup>a</sup> Corrected temp. is the temperature obtained from the measured  $\Delta_{47}$  values using the calibration of Ghosh et al. (2006a) corrected to the difference between the temperature calculated this way for the modern speleothem sample and the modern day bedrock temperature (8 °C offset).

<sup>b</sup> d-excess is estimated using the  $\delta^{18}\text{O}_{\text{water}}$  values in this table and the  $\delta D$  values observed in fluid inclusions as reported by McGarry et al. (2004).

Furthermore, our temperature estimate for the LGM and 56 Ky is close to the sea surface temperatures estimated in the Eastern Mediterranean using alkenone unsaturation ratios (Fig. 1), where LGM temperatures are 10–12 °C and 56 Ky BP temperatures are 14–15 °C in cores M40-4/71 and M40-4/67, located to the south of Crete (based on Fig. 2 in Emeis et al., 2003). Most importantly, these two independent constraints confirm our finding that speleothem growth occurred at temperatures 6–7 °C below modern day bedrock temperatures during the LGM and 3 °C below modern day temperatures at 56 Ky BP; i.e., even though there are clear non-equilibrium effects on the 'clumped isotope' thermometer for speleothems, our assumption of a constant offset of  $\sim 8$  °C between apparent and real temperatures appears to be justified, and the relative changes in temperature through time seem to be faithfully recorded.

The range of early Holocene temperatures we obtain is slightly above modern day temperatures and similar to the sea surface temperatures estimated for that time period using alkenones associated with Eastern Mediterranean Sapropel layer deposition (8–10 Ky from Fig. 2 in Emeis et al., 2003) where the temperatures during this period in cores M40-4/71 and M40-4/67 are 17–21 °C.

Our temperature estimate for the late Holocene samples is the same as modern day temperatures for the 0.9 Ky BP sample. This is slightly lower, though within error, than the temperature range estimated using fluid inclusion  $\delta D$ – $\delta^{18}O$  systematics for this sample. For the sample spanning the time range of 0.9 to 1.9 Ky BP, however, we obtained a temperature of  $14 \pm 1$  °C, significantly below the modern day temperature. The temperature obtained for this sample is lower than seems reasonable for this time period, and is driven by one of the  $CO_2$  extraction replicates whose  $\Delta_{47}$  value is significantly higher. Although omitting the data of that extraction would bring the temperature reflected by this sample to a more reasonable value of 17 °C, there is no obvious reason to reject this data. Eastern Mediterranean alkenone unsaturation data is not available for 1 Ky BP, but the data of Emeis et al. (2003) indicate a sharp trend of decreasing temperatures after the 8–10 Ky BP peak, in accordance with the possible temperature decrease we observe between early and late Holocene.

In general, temperature estimates from alkenones and this study of 'clumped isotope' thermometry agree with each other and are mostly  $\sim 0$ –4 °C higher than the temperatures estimated from combined  $\delta D$ – $\delta^{18}O$  systematics (which is typically within the error estimate reported for the  $\delta D$  measurements). This difference is smaller than recognized external errors of these various techniques, so we conclude that all the available data point to a coherent climate record and that our empirical correction of the 'clumped isotope' thermometer for speleothems is as robust as the independent methods to which we compare it.

#### 4.3. Isotopic composition of cave water

The temperatures estimated using  $\Delta_{47}$  thermometry can be used to assess the  $\delta^{18}O$  values of cave water from the measured  $\delta^{18}O$  of the carbonate and previous calibration

of the temperature-dependent carbonate-water fractionation (modified Kim and O'Neil (1997); as described in Section 2). These data are given in Table 3 and Fig. 2. The  $\delta^{18}O$  value of the carbonate in the modern speleothem sample reflects equilibrium with cave water at 18 °C whose  $\delta^{18}O$  value is  $-4.27 \pm 0.14$ ‰ (the error estimate is based on the error of the temperature estimate, assuming that the contribution of the  $\delta^{18}O_{\text{carbonate}}$  measurement error,  $\pm 0.04$ ‰, is negligible). This value is within the range of water measured in the cave ( $-3.5$  to  $-6.3$ ‰; Bar-Matthews et al., 1996), though more enriched than the  $\delta^{18}O$  values observed for the particular drip water ( $-5.32 \pm 0.76$ ‰ (Bar-Matthews et al., 1996; Ayalon et al., 1998) and see discussion in Section 4.1 above). Our estimated  $\delta^{18}O$  values for cave water during the LGM are higher by approximately 1.1‰ than this modern value. Holocene  $\delta^{18}O$  values are lower than the modern value; by 0.6‰ for the late Holocene and by 1.0‰ for the early Holocene samples. At 56 Ky BP, the  $\delta^{18}O$  value of cave water ( $-4.01 \pm 0.28$ ‰) is slightly higher than the modern water, and is intermediate between LGM and late Holocene values.

Given the slight temperature variation during the early and late Holocene, the change in  $\delta^{18}O$  values of the speleothem carbonate can be fully attributed (within error) to variation in  $\delta^{18}O$  values of cave water. About half of the change in  $\delta^{18}O_{\text{carbonate}}$  between the modern and the LGM can be attributed to change in water composition and the remainder is due to temperature change. About three quarters of the difference in  $\delta^{18}O_{\text{carbonate}}$  between the modern and 56 Ky BP can be attributed to change in temperature.

The  $\delta D$  values in fluid inclusions can be combined with our estimates of cave water  $\delta^{18}O$  values to assess the d-excess parameters (Table 3 and Fig. 3). Modern day rain and cave water in Soreq has d-excess values that are significantly higher than that of the Global Meteoric Water Line (GMWL, d-excess = 10‰) and plot around a local

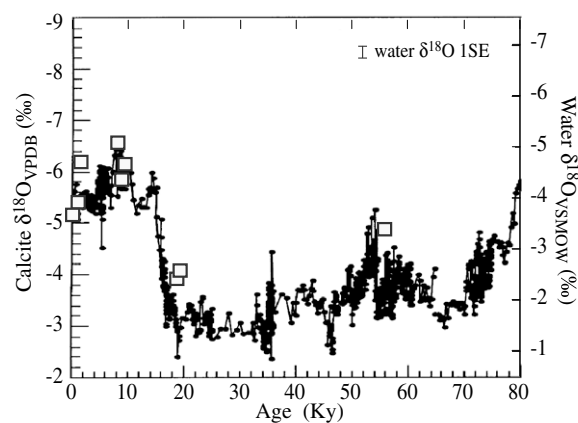


Fig. 2.  $\delta^{18}O$  of cave water (gray squares) as deduced from the  $\delta^{18}O_{\text{carbonate}}$  values and temperatures obtained in this study compared to  $\delta^{18}O$  of speleothems carbonate as adapted from Matthews et al. (2000). Carbonate values are given using the VPDB scale. Water values are given using the VSMOW scale. Note that the  $\delta^{18}O_{\text{water}}$  scale is shifted by 1.5‰ with respect to the carbonate scale. The error bar is the typical ISE of  $\delta^{18}O_{\text{water}}$  based on the temperature error estimate.

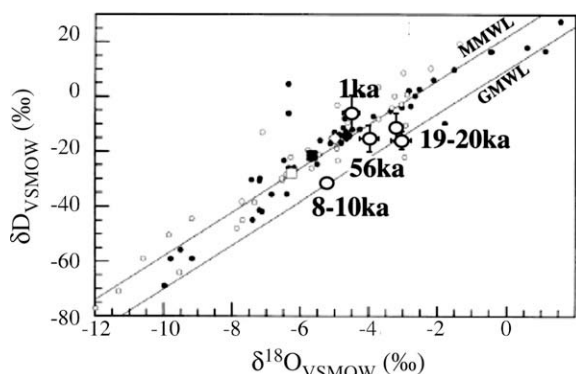


Fig. 3.  $\delta^{18}\text{O}$ - $\delta\text{D}$  relationship of the cave water associated with the samples measured in this study (large gray circles, with the date associated with the samples given near the symbols) compared to the meteoric water line and local rain water (small circles; Bar-Matthews et al., 2003).  $\delta^{18}\text{O}$  values are from this study,  $\delta\text{D}$  values are from McGarry et al. (2004). Both are given using the VSMOW scale. GMWL refers to the global meteoric water line. MMWL refer to the local Mediterranean meteoric water line.

Mediterranean Meteoric Water Line (MMWL; d-excess of  $\sim 20\text{‰}$  (Gat and Carmi, 1970; Gat, 1996; Gat et al., 2003)). The late Holocene sample has a d-excess value of  $30.1\text{‰}$  and plots within the range of modern day rain. The two LGM samples have d-excess values of  $8.5\text{‰}$  and  $14.4\text{‰}$  and both plot within error on the GMWL. These values are lower than those previously estimated for these particular samples but are similar to d-excess values estimated for other LGM samples in Soreq (McGarry et al., 2004). Thus, our results independently confirm the hypothesis of McGarry et al. that LGM precipitation near Soreq cave was close to the GMWL. The 56 Ky sample has a d-excess value of  $16.7\text{‰}$ , placing it between the GMWL and MMWL, as expected from its intermediate climatic conditions, and within the range estimated previously (McGarry et al., 2004). The early Holocene sample has a d-excess value of  $10.5\text{‰}$ , significantly lower than estimated by McGarry et al. (2004), putting it on the GMWL.

The d-excess is a measure of the kinetic isotope fractionation during evaporation and water vapor formation and is typically interpreted as a measure for relative humidity above the sea (Gat, 1996). The shift to low d-excess values during the LGM could either be the result of the decrease in temperature or an increase in relative humidity and is probably a combination of both. McGarry et al. (2004) noted that a relative humidity of 45% would result in a modern day d-excess value ( $\sim 20\text{‰}$ ) at  $20\text{ °C}$  but would give lower d-excess at lower temperatures ( $\sim 10\text{‰}$  at  $0\text{ °C}$ ). Using these variations (as given in Fig. 1 of McGarry et al., 2004), we estimate that the average d-excess of  $11.5\text{‰}$  at an average temperature of  $11.7\text{ °C}$  in the LGM reflects a relative humidity value of  $\sim 60\%$ . A similar analysis gives a relative humidity value of  $\sim 50\%$  for the 56 Ky sample and close to 70% for the early Holocene sample.

Variations in  $\delta^{18}\text{O}$  values in cave water are typically interpreted as reflecting variations in the isotopic composition of the source, and in the amount of rainfall. Temperature estimates obtained from ‘clumped isotopes’

measurements may assist (together with d-excess) in an analysis of rainfall patterns, considering both temperature and relative humidity variations to account for changes in the atmospheric moisture content. However, given the current uncertainties concerning isotopic dis-equilibrium in speleothems, we believe it is premature to provide a full climatic interpretation. Future work is needed to fully characterize the controlling mechanisms of ‘clumped isotopes’ dis-equilibrium in speleothem, in order to allow for such interpretation.

## 5. CONCLUSIONS

The recently developed ‘clumped isotopes’ thermometry technique was applied here to speleothem samples precipitated during the Holocene and last glacial period in Soreq cave in Israel as a feasibility test for the applicability of this method to speleothems. After applying an empirical correction for an offset associated with a kinetic isotope effect that is particular to the ‘clumped isotope’ compositions of speleothems, Holocene temperatures were found to be similar to modern day, with the late Holocene time around 1 Ky BP being a little cooler and the Early Holocene time between 7 and 10 Ky BP, a little warmer. The temperatures during the last glacial maximum were  $6\text{--}7\text{ °C}$  cooler than the modern day temperatures. Intermediate temperatures were observed earlier in the last glacial, at 56 Ky BP. These cave temperatures at Soreq are close to Eastern Mediterranean sea surface temperatures, estimated previously using alkenone unsaturation levels (Emeis et al., 2003), suggesting that continental variations are similar to nearby marine conditions.

These temperatures were used to partition the effect of temperature and water isotopic composition on the  $\delta^{18}\text{O}$  values of the speleothem carbonate, indicating that cave water  $\delta^{18}\text{O}$  at the late Holocene was rather similar to modern day, early Holocene water was  $\sim 1\text{‰}$  more depleted, and the last glacial maximum water were  $\sim 1.1\text{‰}$  more enriched whereas the 56 Ky BP again reflected intermediate values.

In conjunction with previously reported fluid inclusion  $\delta\text{D}$  data (McGarry et al., 2004), d-excess was estimated to be similar to modern day during the late Holocene, plotting on the local Mediterranean Meteoric Water Line. Early Holocene and last glacial maximum d-excess was significantly lower, plotting on the Global Meteoric Water Line, and implying a significantly higher relative humidity compared to modern day conditions. The 56 Ky sample plotted between the two lines, with a relative humidity that is slightly higher than modern day.

This work provided a test for the applicability of the ‘clumped isotope’ thermometry technique for temperature reconstruction using speleothems. It seems like the method is suitable, though one has to be careful and utilize only speleothems that were deposited at close to equilibrium conditions, as the temperature reconstruction seem overly sensitive to kinetic isotope effects. The results indicated that this affects mainly the absolute temperatures obtained whereas the differences among samples are much less sensitive. Therefore, comparison with modern speleothem



samples that were formed at similar precipitation conditions and at a known temperature is highly recommended. Future work should test specifically the effect of thin film precipitation on  $\Delta_{47}$  values and perform a full calibration of the 'clumped isotopes' thermometry scale for speleothems.

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