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**Key Points:**
- We use dual clumped isotope thermometry ($\Delta_{47}$ and $\Delta_{48}$) to test for changes in calcite $\delta^{18}O$ unrelated to variations in $\delta^{18}O$ of groundwater
- Calcite $\delta^{18}O$ record represents changes solely in $\delta^{18}O$ of groundwater without contributions from variations in temperature and kinetics
- It is possible to achieve a stable carbonate precipitation environment over long timescales

# Devils Hole Calcite Was Precipitated at ±1°C Stable Aquifer Temperatures During the Last Half Million Years

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**Abstract** Subaqueous carbonates from the Devils Hole caves (southwestern USA) provide a continuous Holocene to Pleistocene North American paleoclimate record. The accuracy of this record relies on two assumptions: That carbonates precipitated close to isotope equilibrium and that groundwater temperature did not change significantly in the last 570 thousand years. Here, we investigate these assumptions using dual clumped isotope thermometry. This method relies on simultaneous analyses of carbonate $\Delta_{47}$ and $\Delta_{48}$ values and provides information on the existence and extent of kinetic isotope fractionation. Our results confirm the hypothesis that calcite precipitation occurred close to oxygen and clumped isotope equilibrium during the last half million years in Devils Hole. In addition, we provide evidence that aquifer temperatures varied by less than ±1°C during this interval. Thus, the Devils Hole calcite $\delta^{18}O$ time series exclusively represents changes in groundwater $\delta^{18}O$ values.

**Plain Language Summary** The oxygen isotope composition of cave carbonates records changes in Earth's climate. However, the reliability of such records depends on how stable the carbonate precipitation environment was. Here, we use a novel method called dual clumped isotope thermometry that can provide simultaneous information on a carbonate's growth temperature and whether any additional fractionation processes affected its oxygen and clumped isotope signatures. Specifically, we investigated the Devils Hole caves, which provide a reference oxygen isotope time series for North America. We find that groundwater temperature did not change significantly in the last half-million years. Variations in the oxygen isotope composition of the deposited carbonates solely reflect variations in the oxygen isotope composition of the groundwater.

## 1. Introduction

The oxygen isotope composition of cave carbonates ($\delta^{18}O_{cc}$) is a common tool to reconstruct terrestrial climate (Comas-Bru et al., 2020; Fairchild & Baker, 2012). In particular, speleothems are the primary source of information on Quaternary climatic variability of the Great Basin, southwestern United States (Coplen et al., 1994; Lachniet et al., 2011, 2014; 2020; Moseley et al., 2016; Quirk et al., 2020; Shakun et al., 2011; Wendt et al., 2018; Winograd et al., 1988, 1992, 2006). Subaqueously formed folia-free mammillary calcites from the Devils Hole groundwater system (Figure 1) provide a unique, uninterrupted $\delta^{18}O_{cc}$ record between 4.5 and 570 ka (Winograd et al., 1988, 1992, 2006). In thermodynamic equilibrium, the $\delta^{18}O_{cc}$ value is only a function of the carbonate precipitation temperature and the groundwater oxygen isotope composition ($\delta^{18}O_{gw}$). Assuming that the aquifer's temperature did not vary with time and that carbonate growth occurred close to isotope equilibrium, the reconstructed Devils Hole $\delta^{18}O_{gw}$ time series is thought to reflect changes in meteoric precipitation.

The well-dated Devils Hole record, while showing an excellent agreement with California Current's sea surface temperatures (Herbert et al., 2001; Winograd et al., 2006), displays transitions to interglacial periods ca. 10,000 years before orbital forcing would predict (Ludwig et al., 1992, 1988, 1992, 2006). This age discrepancy is not reproduced in other speleothem records from the Great Basin (Lachniet et al., 2011, 2014; 2020). A revised chronology of the Devils Hole $\delta^{18}O$ time series—based on newly recovered material—suggests that excess $^{230}Th$ in the water column, originating from the radioactive decay of $^{234}U$, leads to uranium-series
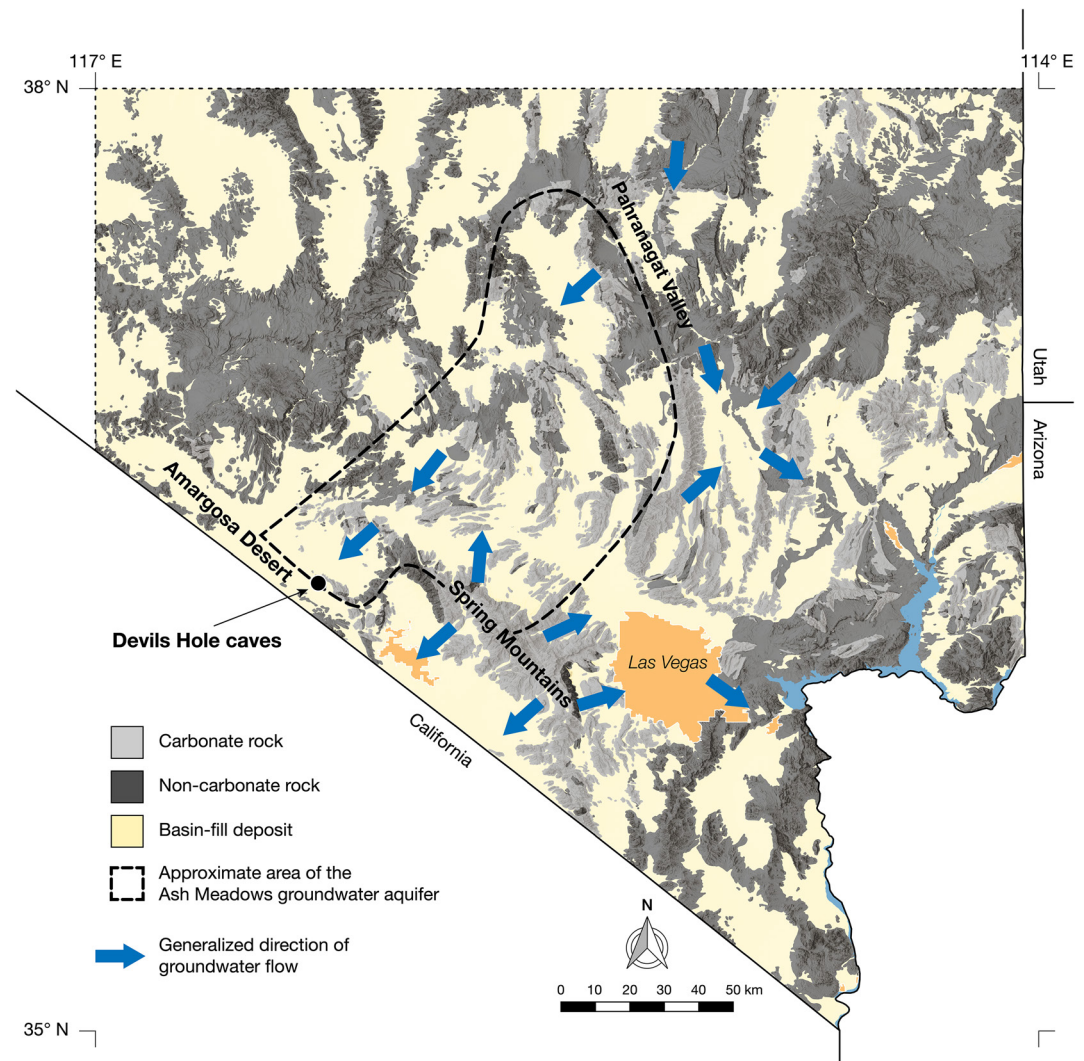
**Figure 1.** Location of the Devils Hole caves in southern Nevada. The map shows the Ash Meadows groundwater aquifer (dashed line) and approximate groundwater flow directions (blue arrows) (Thomas et al., 1996) over the region's generalized geology (Denny & Drewes, 1965; Horton et al., 2017).

ages that are too old (Moseley et al., 2016). Alternatively, variations in the temperature of the subaqueous environment and the kinetics of carbonate mineralization could result in a $\delta^{18}O_{cc}$ record that does not accurately represent changes in $\delta^{18}O_{gw}$ and, thus, could contribute to the apparent age discrepancy.

Multiple lines of indirect evidence suggest both a stable subaqueous temperature and close to equilibrium calcite precipitation conditions for most of the Devils Hole record (Coplen, 2007). The Devils Hole caves formed tectonically at the Ash Meadows groundwater aquifer's fault-controlled discharge area (Riggs et al., 1994) (Figure 1). The partially submerged caverns provided an isolated carbonate growth environment. When the caves opened to the surface, mammillary calcite formation ceased (Plummer et al., 2000). Based on the large size of the Ash Meadows aquifer (>12,000 km²), the groundwater temperature has been postulated to remain constant on longer timescales. Kinetic isotope fractionation in most speleothems is related to the degassing of $CO_{2\,(aq)}$ from the groundwater (Affek et al., 2008; Affek & Zaarur, 2014; Daëron et al., 2011; El-Shenawy et al., 2020; Fairchild & Baker, 2012; Guo & Zhou, 2019; Hansen et al., 2013; Hendy, 1971; Kluge & Affek, 2012; Kluge et al., 2014). The mammillary calcites in the Devils Hole caves exhibit growth rates below 1.5 mm kyr⁻¹ (Winograd et al., 2006), orders of magnitude slower than growth rates of subaerial speleothems. Due to these slow growth rates, the DIC-$H_2O$-$CaCO_3$ system (dissolved inorganic carbon (DIC)) may have had sufficient time to attain isotope equilibrium (Dreybrodt & Scholz, 2011;

Winograd et al., 1992). Previous clumped isotope measurements ($\Delta_{47}$) from Devils Hole Cave 2 hinted at a stable (30.6 ± 2.6°C) groundwater temperature between 65 and 180 ka (Kluge et al., 2014), corroborating that $\delta^{18}O_{cc}$ values predominantly record variations in $\delta^{18}O_{gw}$ values. However, like their oxygen isotope composition, the clumped isotope composition of carbonates can also be affected by kinetic fractionation (Bajnai et al., 2020; Daëron et al., 2011, 2019; Guo & Zhou, 2019). The $\Delta_{47}$ and $\delta^{18}O_{cc}$ measurements alone do not allow one to resolve potential kinetic effects in carbonate formation temperatures, especially in terrestrial environments where the $\delta^{18}O$ values of the parent fluid are highly variable. Without independent evidence for insignificant contributions of reaction kinetics to the clumped and oxygen isotope record, the inferred temperature stability remains uncertain.

Recent developments in mass spectrometry enable simultaneous, high-precision analysis of the mass-48 $CO_2$ isotopologue (mostly $^{12}C^{18}O^{18}O$; $\Delta_{48}$) and the mass-47 $CO_2$ isotopologue (mostly $^{13}C^{18}O^{16}O$; $\Delta_{47}$), derived from carbonate minerals (Fiebig et al., 2019). In $\Delta_{47}$ versus $\Delta_{48}$ space, thermodynamic equilibrium at any given temperature is represented by a single point. Deviations from thermodynamic isotope equilibrium related to temporal variations in reaction kinetics proceed along trajectories specific to the underlying reaction mechanisms, for example, $CO_{2\,(aq)}$ degassing (Guo, 2020; Guo & Zhou, 2019). Simultaneous $\Delta_{48}$ and $\Delta_{47}$ measurements on a single carbonate phase, termed dual clumped isotope thermometry, enable identifying the nature and extent of kinetics involved in carbonate mineralization (Bajnai et al., 2020).

In this study, we analyzed the $\Delta_{47}$ and $\Delta_{48}$ values of 10 mammillary calcites from the Devils Hole caves spanning the last half million years. We investigated the potential relevance of kinetically induced variations on $\delta^{18}O_{cc}$ values and whether variable reaction kinetics and crystallization temperatures could affect the accuracy of the time series.

## 2. Materials and Methods

### 2.1. Study Area and Materials

We investigated mammillary calcites from the Devils Hole (36.425355°N, 116.291447°W) and the Devils Hole Cave 2 (36.427122°N, 116.291166°W) subaqueous caves, situated in the Amargosa Desert, Nevada, USA (Figure 1). Both caves formed tectonically in Cambrian carbonates and dolomites (Riggs et al., 1994; Winograd & Thordarson, 1975). The aquifer recharges from two sources: Over 60% of the groundwater originates from the nearby Spring Mountains, ca. 80 km to the northeast, and up to 40% of the groundwater comes from the Pahranagat Valley, ca. 140 km to the north (Thomas et al., 1996). Based on $^{14}C$ ages, the groundwater travel time is estimated to be 2,200 years and 5,900 years, respectively (Thomas et al., 1996). The primary source of recharged water in the Spring Mountains is snowmelt (Winograd et al., 1998). The $\delta^{18}O$ values of modern winter meteoric precipitation in southern Nevada range from −12.5‰ to −14.5‰ (Ingraham et al., 1991).

Material for this study was cut from the three cores studied by Coplen (2007); Winograd et al. (1988), (1992), (2006). These cores were explicitly chosen as they pertain to the original Devils Hole time series. Core DH-11 is from Devils Hole, and cores DHC2-8 and DHC2-3 are from Devils Hole Cave 2. There are no measurable differences between the two caves, neither in modern groundwater temperature nor in contemporaneous $\delta^{18}O_{cc}$ values (Winograd et al., 2006). The three cores were retrieved from 60 to 20 m below the present water level. The water level in the caves dropped by ca. 9 m since the last glacial period, which has been linked to changes in regional moisture availability (Szabo et al., 1994; Wendt et al., 2018). However, in the cores studied here, there are no folia and there is no evidence for dissolution, recrystallization, or any depositional hiatus (Kolesar & Riggs, 2004), indicating that they were continuously submerged since the middle Pleistocene. For clarification, we note here that Kluge et al. (2014) and Moseley et al. (2016) investigated cores containing interlayered folia and mammillary calcite from Devils Hole Cave 2, which were collected at or above the modern water table; they are different from those studied here, which were formed more than 20 m below the modern water table. The calcite slabs, taken from the cores, were first cleaned in an ultrasonic bath using de-ionized water, dried in a vacuum oven at 30°C, and finally homogenized using an agate mortar and pestle.

**Table 1**
*Results of Dual Clumped Isotope Thermometry on Devils Hole Calcites*

| Sample | Cave | Age interval (ka) | Replicates | $\Delta_{47\,(CDES90)}$ (‰) | $\Delta_{48\,(CDES90)}$ (‰) |
|---|---|---|---|---|---|
| DHC2-8 | Devils Hole Cave 2 | 4.5–16.9 | 14 | 0.573 (±0.003) | 0.237 (±0. 016) |
| DHC2-3 | Devils Hole Cave 2 | 32.2–39.8 | 9 | 0.575 (±0.007) | 0.227 (±0.019) |
| DH-11 19.7 | Devils Hole | 86.4–94.3 | 9 | 0.572 (±0.003) | 0.229 (±0.020) |
| DH-11 44.5 | Devils Hole | 121.8–123.7 | 12 | 0.581 (±0.005) | 0.210 (±0.018) |
| DH-11 73.0 | Devils Hole | 176.1–184.8 | 9 | 0.575 (±0.006) | 0.225 (±0.017) |
| DH-11 109.4 | Devils Hole | 232.8–240.5 | 23 | 0.575 (±0.003) | 0.208 (±0.011) |
| DH-11 141.6 | Devils Hole | 291.3–299.0 | 9 | 0.570 (±0.005) | 0.208 (±0.022) |
| DH-11 189.9 | Devils Hole | 353.0–358.3 | 14 | 0.574 (±0.005) | 0.217 (±0.014) |
| DH-11 201.3 | Devils Hole | 371.7–388.4 | 9 | 0.568 (±0.007) | 0.226 (±0.022) |
| DH-11 296.6 | Devils Hole | 485.5–507.8 | 8 | 0.575 (±0.005) | 0.222 (±0.022) |
| | | | **Average** | **0.574 (±0.003)** | **0.221 (±0.007)** |

*Note.* The age intervals of the samples analyzed in this study correspond to the chronology of Winograd et al. (2006) (see also Landwehr et al. (2011)). The uncertainties represent 95% confidence intervals (Fernandez et al., 2017).

### 2.2. Dual Clumped Isotope Thermometry

Clumped isotope analyses were performed on a Thermo Scientific 253 Plus gas source isotope ratio mass spectrometer connected directly to a fully automated carbonate acid digestion system (90°C) and $CO_2$ purification line, detailed in Fiebig et al. (2019). The samples were measured along with carbonate standards (ETH-1, ETH-2, and ETH-3) in two sessions between September 2019 and June 2020. To complement the measurements in this study, we included five replicate analyses of sample DHC2-8 reported in Bajnai et al. (2020), thus, all samples were measured in 9–23 replicates. The clumped isotope values were calculated using the IUPAC isotope parameters (Brand et al., 2010; Daëron et al., 2016) and are reported on the carbon dioxide equilibrium scale at 90°C (indicated by subscript "CDES90"). Data correction of the carbonate samples for all measurement periods consisted of three steps, that is, correction for non-linearity, correction for scale compression, and correction for variation in the acid reaction environment, similarly as described in Bajnai et al. (2020). An extended description of the data processing steps is provided in the supporting information. All data of the analyses of both samples and reference materials are provided in Datasets S1–S2.

### 3. Results

The $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values of the 10 investigated Devils Hole samples are listed in Table 1. There is no covariation between the $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values of the samples ($N = 10$, $R^2 < 0.1$, $p >> 0.05$). Moreover, all samples have $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values indistinguishable within their 95% confidence intervals (Figure 2). The mean $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values of the 10 samples are 0.574(±0.003)‰ and 0.221(±0.007)‰, respectively (Figure 2, Table 1).

### 4. Discussion

The groundwater temperature in the caves has been remarkably invariant in the last 80 years. For March 1985, the most precise measurement published up to date reports 33.7(±0.2)°C in the main chamber of Devils Hole at depths between 5 and 37.5 m below water level (Plummer et al., 2000). This value is in good agreement with temperatures reported for November 1954, ranging from 33.9°C to 34.0°C (at 2–29 m below the modern water table), and for April 1961, ranging from 34.0°C to 34.3°C (at 1.3–27 m below the water table) (Hoffman, 1988). Earlier studies reported similar temperatures, that is, 32.8°C–33.9°C for the 1930–1947 period (Miller, 1948), and 33.5°C for December 1966 (Dudley & Larson, 1974). Furthermore, the covariation of fluid inclusion $\delta^2H$ and $\delta^{18}O_{cc}$ values hint at constant temperatures through the penultimate full glacial and peak interglacial (Winograd et al., 1992). Specifically, the difference in the $\delta^2H$ values of
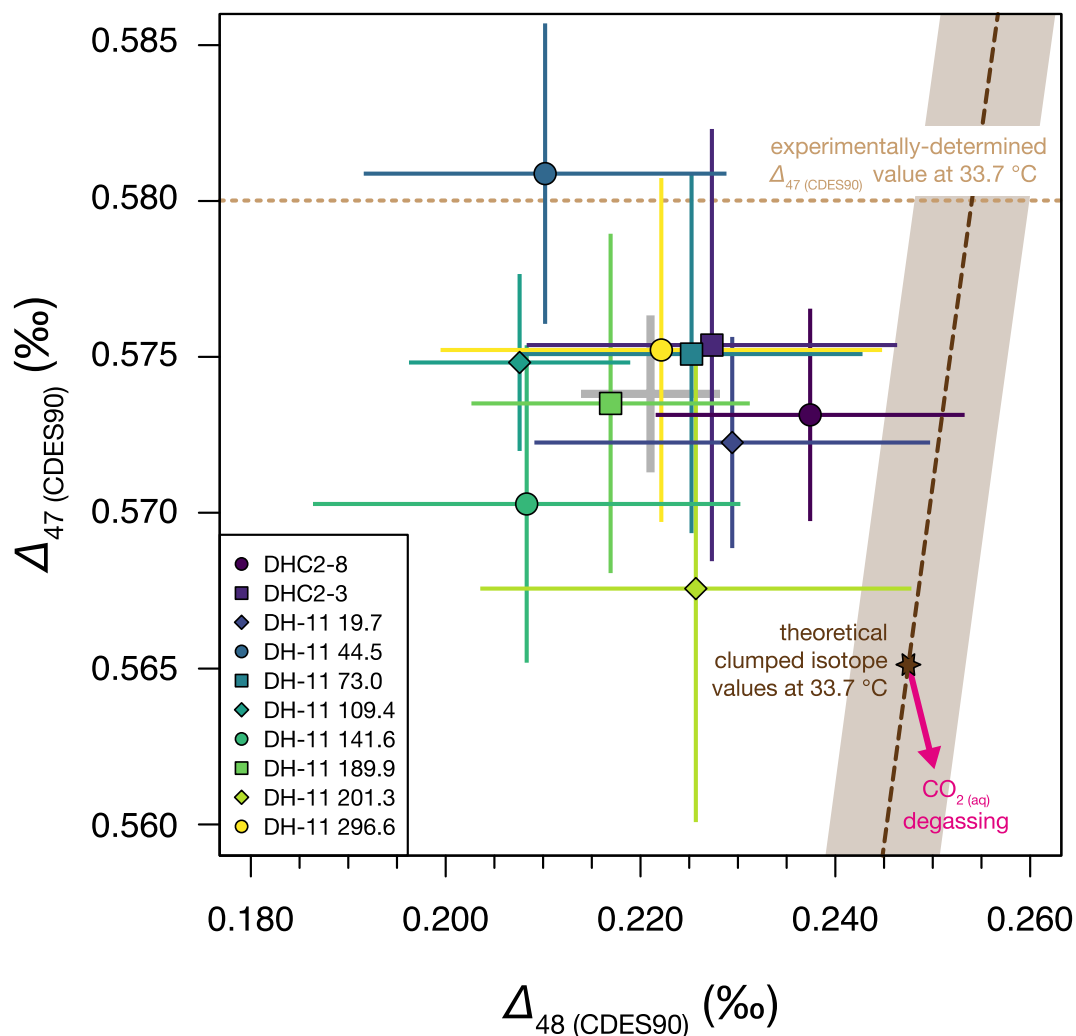
**Figure 2.** $\Delta_{48 \, (CDES90)}$ and $\Delta_{47 \, (CDES90)}$ values of subaqueous vein calcites from the Devils Hole caves. There is no correlation among the data. The sample values are indistinguishable from each other, providing direct evidence for a kinetically and thermally invariable precipitation environment. The brown shaded area depicts the uncertainty of the theoretical clumped isotope calibration. The pink arrow shows the trajectory (slope: −1.261) of the approximately linear early departure from apparent equilibrium $\Delta_{48 \, (CDES90)}$ and $\Delta_{47 \, (CDES90)}$ values at 33.7°C (brown star) introduced by $CO_{2 \, (aq)}$ degassing (Bajnai et al., 2020; Guo & Zhou, 2019). The colored error bars indicate the 95% confidence interval of the replicate measurements. The gray cross indicates the mean value of all Devils Hole samples and the corresponding 95% confidence interval.

water trapped in 130 and 160 ka old mammillary calcites, respectively, is 14(±2)‰ (Winograd et al., 1992). According to the local winter meteoric water line ($\delta^2$H = 7.47 × $\delta^{18}$O + 2.84 (Lachniet et al., 2020)), such difference in $\delta^2$H values can fully explain the corresponding 1.65(±0.07)‰ change in $\delta^{18}O_{cc}$ values solely related to $\delta^{18}O_{gw}$ at a constant carbonate growth temperature (Coplen, 2007; Winograd et al., 1992). During the deposition of the most recent sample DHC2-8 (4.5–16.9 ka), the $\delta^{18}O_{cc}$ values remained constant (within ±0.1‰), and the calcite growth rate did not exceed 0.2 mm kyr$^{-1}$ (Coplen, 2007; Winograd et al., 2006). The groundwater's temperature when DHC2-8 precipitated is thought to be identical to its modern temperature (33.7°C) (Coplen, 2007). Overall, the clumped and oxygen isotope compositions of DHC2-8 are considered to best represent equilibrium values at 33.7°C among Earth-surface carbonates (Coplen, 2007; Daëron et al., 2019; Tripati et al., 2015; Wostbrock et al., 2020).

The precipitation temperature and the potential importance of kinetics can be independently investigated using dual clumped isotope thermometry (Bajnai et al., 2020; Fiebig et al., 2019; Guo, 2020; Guo &

Zhou, 2019). A robust $\Delta_{47\,(CDES90)}$ versus temperature calibration was obtained by reprocessing $\Delta_{47}$ data from multiple experimental studies using a unique set of isotope parameters required for data evaluation (Petersen et al., 2019). An experimental temperature calibration is not yet available for $\Delta_{48\,(CDES90)}$ values. To obtain a first estimate of the equilibrium temperature dependence of $\Delta_{48\,(CDES90)}$, one can combine theoretically computed equilibrium $\Delta_{64}$ values of calcite (Hill et al., 2014) with the experimentally determined calcite-$CO_2$ acid fractionation factor of 0.138($\pm$0.005)‰ (Bajnai et al., 2020). A corresponding theoretical $\Delta_{47}$ versus temperature relationship is obtained similarly by adding the experimentally determined calcite-$CO_2$ acid fractionation factor of 0.194 ($\pm$0.002)‰ (Bajnai et al., 2020) to the theoretical $\Delta_{63}$ values (Hill et al., 2014).

Figure 2 compares the measured $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values with the corresponding theoretical and experimental equilibrium values at 33.7°C. Notably, the measured $\Delta_{47\,(CDES90)}$ value of DHC2-8 (0.573 $\pm$ 0.003‰) falls into a boundary range defined by the experimental (0.580‰; the error of the calibration is <0.001‰) (Petersen et al., 2019) and the theoretical (0.565 $\pm$ 0.002‰) (Bajnai et al., 2020; Hill et al., 2014) equilibrium values at 33.7°C (Figure 2). Similarly, the theoretical equilibrium $\Delta_{48\,(CDES90)}$ value at 33.7°C (0.248 $\pm$ 0.005‰) is within the confidence interval of the measured $\Delta_{48\,(CDES90)}$ value of DHC2-8 (0.237 $\pm$ 0.019‰). These observations support the hypothesis that DHC2-8 precipitated in or close to thermodynamic equilibrium at 33.7°C.

However, it needs to be considered that the exact position of equilibrium in $\Delta_{47\,(CDES90)}$ versus $\Delta_{48\,(CDES90)}$ space is not yet known with confidence, as the discrepancy between the theoretical and the experimental equilibrium $\Delta_{47\,(CDES90)}$ values at 33.7°C indicate. Within their 95% confidence interval, the measured $\Delta_{48\,(CDES90)}$ and $\Delta_{47\,(CDES90)}$ values of most samples from the Devils Hole caves are indistinguishable from the corresponding values of sample DHC2-8 (Figure 2; although sample DH-11 109.4 shows a 0.002‰ difference in its $\Delta_{48\,(CDES90)}$ value from the value of DHC2-8, this minor difference is likely a result of statistical uncertainty, that is, arising from the 5% probability that both samples have indistinguishable $\Delta_{48\,(CDES90)}$, especially because the $\Delta_{47\,(CDES90)}$ values of these two samples are indistinguishable from each other; Figure 2). However, unlike DHC2-8, all other samples plot slightly above the theoretical $\Delta_{47\,(CDES90)}$ versus $\Delta_{48\,(CDES90)}$ equilibrium line (Figure 2). If kinetics prevailed, these would be associated with $CO_{2\,(aq)}$ degassing from the groundwater rather than $CO_2$ absorption (Kluge et al., 2014). Theoretical modeling and experimental results indicate that $CO_{2\,(aq)}$ degassing simultaneously shifts $\Delta_{47}$ values toward lower and $\Delta_{48}$ values toward higher values with increasing growth rates (Bajnai et al., 2020; Guo, 2020; Guo & Zhou, 2019). Therefore, if involved, $CO_{2\,(aq)}$ degassing kinetics should cause departures below the equilibrium line, contrary to what is observed (Figure 2). This conundrum implies that the theoretical calibration overestimates the equilibrium $\Delta_{48\,(CDES90)}$ values. Unless the thermodynamic equilibrium $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values at 33.7°C are accurately determined, it is impossible to provide definitive evidence that DHC2-8 and all other samples attained full internal equilibrium at 33.7°C.

If temperature variations have occurred in the Devils Hole caves, one could expect them between peak glacial and interglacial periods. For this reason, we investigated samples DH-11 44.5 and DH-11 189.9, representing the maximum and the minimum of the Devils Hole $\delta^{18}O_{cc}$ time series, that is, periods of interglacial and glacial maxima, respectively (Figure 3a). Despite the presumably maximum surface temperature spread, the $\Delta_{47\,(CDES90)}$ and the $\Delta_{48\,(CDES90)}$ values of these two samples remain indistinguishable (Figure 2, Table 1). The lack of systematic variation in the measured $\Delta_{48\,(CDES90)}$ and $\Delta_{47\,(CDES90)}$ values, together with the observation that all samples are indistinguishable from each other in $\Delta_{47\,(CDES90)}$ versus $\Delta_{48\,(CDES90)}$ space, strongly implies that reaction kinetics related to $CO_{2\,(aq)}$ degassing—if having been effective at all—were invariant during the formation of the half-million-year-long Devils Hole record. An alternative scenario would require that temperature and kinetic effects compensated each other. Considering the effects of temperature and $CO_{2\,(aq)}$ degassing kinetics on $\Delta_{47\,(CDES90)}$, $\Delta_{48\,(CDES90)}$, and $\delta^{18}O_{cc}$, one can demonstrate that such a scenario is unreasonable. For example, a 2°C decrease in temperature, that is, from 34°C to 32°C, would correspond with shifts of +0.005‰ in $\Delta_{47\,(CDES90)}$ and +0.002‰ in $\Delta_{48\,(CDES90)}$ based on the theoretical calibration (Bajnai et al., 2020; Hill et al., 2014), and with a shift of +0.38‰ in $\delta^{18}O_{cc}$ based on Coplen (2007). Because the temperature sensitivity of the $\Delta_{47}$ and $\delta^{18}O$ versus temperature calibrations, respectively, are roughly consistent, the choice of calibrations has only a minimal effect (on the order of 0.01‰ for $\delta^{18}O$ and 0.001‰ for $\Delta_{47}$) on the calculated values. To fully compensate the temperature-related positive $\Delta_{47\,(CDES90)}$
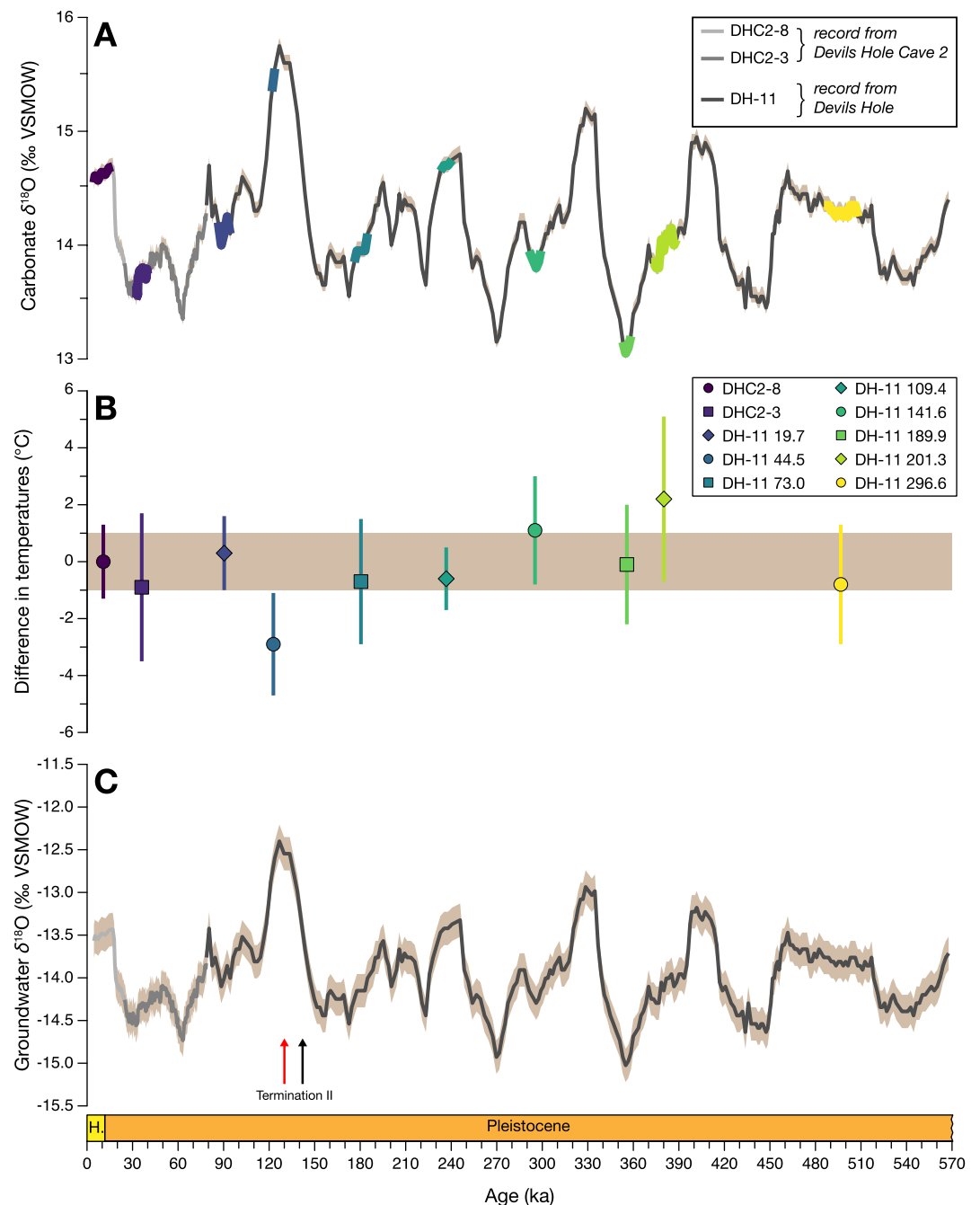
**Figure 3.** Dual clumped isotope thermometry reveals stable calcite precipitation temperatures in the Devils Hole caves. (a) Carbonate $\delta^{18}$O record from Devils Hole and Devils Hole Cave 2 (Winograd et al., 2006). The colored sections correspond to the age range of the samples in this study (Table 1). The range of the $\delta^{18}O_{cc}$ values in the sampled intervals is less than 0.35‰. The analytical uncertainty of the $\delta^{18}O_{cc}$ measurements is ±0.07‰ (shaded area). (b) Differences in the $\Delta_{47}$-derived calcite precipitation temperatures (Petersen et al., 2019) between DHC2-8 (33.7°C) and older samples. The shaded area encloses the 95% confidence interval of the mean $\Delta_{47\,(CDES90)}$ value of all samples, which corresponds to ±1°C. Error bars represent the 95% confidence intervals of the measurements. (c) Groundwater $\delta^{18}$O values, reconstructed using the $\delta^{18}O_{cc}$ values from panel A and 33.7 (±1)°C (Coplen, 2007). The timing of Termination II, that is, the penultimate glacial/interglacial transition, occurs at 142 ka in Devils Hole $\delta^{18}O_{cc}$ record (black arrow) (Winograd et al., 2006) and at 130 ka in the LR04 benthic $\delta^{18}$O stack (red arrow) (Lisiecki & Raymo, 2005).

shift with an opposing negative $\Delta_{47\,(CDES90)}$ shift, $CO_{2\,(aq)}$ degassing kinetics must become more pronounced. Modeling of the $DIC-H_2O-CaCO_3$ system indicates that during the early stages of $CO_{2\,(aq)}$ degassing, carbonate $\Delta_{47\,(CDES90)}$ and $\Delta_{48\,(CDES90)}$ values and $\Delta_{47\,(CDES90)}$ and $\delta^{18}O_{cc}$ values depart from equilibrium along linear trajectories (Guo, 2020; Guo & Zhou, 2019). These modeled trajectories were confirmed by experimental data for $\Delta_{47}$ versus $\delta^{18}O$ (Guo, 2020) and $\Delta_{47}$ versus $\Delta_{48}$ (Bajnai et al., 2020). Based on the environmental conditions of the Devils Hole caves ($T = 33.7°C$, pH = 7.4, (DIC) = 5.35 (Plummer et al., 2000)), the corresponding slopes are −0.027 for $\Delta_{47}$ versus $\delta^{18}O$ and −1.261 for $\Delta_{47}$ versus $\Delta_{48}$ (Guo, 2020; Guo & Zhou, 2019) (Figure 2). Accordingly, a counterbalancing −0.005‰ shift in $\Delta_{47\,(CDES90)}$ would cause additional changes in both $\Delta_{48\,(CDES90)}$ and $\delta^{18}O_{cc}$ by +0.004‰ and +0.19‰, respectively. The coupled effect of +0.006‰ on $\Delta_{48\,(CDES90)}$ is below the analytical precision, but a kinetic compensation of a 2°C cooling would shift $\delta^{18}O_{cc}$ by a total of +0.57‰. Equivalently, the full kinetic compensation of a 2°C warming would affect $\delta^{18}O_{cc}$ by −0.57‰. Consequently, compensation of temperature variations by kinetic effects—if it occurred—would have significantly contributed to the observed $\delta^{18}O_{cc}$ variations, which only span a total range of 2.70‰. However, covariations in fluid-inclusion $\delta^2H$ values and corresponding $\delta^{18}O_{cc}$ values in the Devils Hole record have been observed to satisfactorily fit the local meteoric water line (Coplen, 2007; Winograd et al., 1992).

Because all data points are indistinguishable, one can determine the 95% confidence interval of the mean $\Delta_{47\,(CDES90)}$ values of the samples: ±0.003‰. This $\Delta_{47\,(CDES90)}$ uncertainty translates into a maximum temperature variability of ±1°C around 33.7°C, independent if the experimental (Petersen et al., 2019) or the theoretical calibration (Bajnai et al., 2020; Hill et al., 2014) is used (Figure 3b). During inorganic carbonate precipitation, it is reasonable to expect that the clumped and the oxygen isotope compositions of the carbonates are affected by identical kinetic processes. In the case of Devils Hole, the constant carbonate precipitation environment suggested by the clumped isotope data implies that the $\delta^{18}O_{cc}$ values of the samples are similarly not affected by kinetic variations. The analytical uncertainty of the $\delta^{18}O_{cc}$ measurements of the Devils Hole record is ±0.07‰ (Winograd et al., 2006), and the temperature sensitivity of the oxygen isotope fractionation between calcite and water is 0.19‰°C$^{-1}$ around 30°C, independent of the calibration of choice (Coplen, 2007). Consequently, the observed constant temperatures attest to an extremely stable subaqueous environment and that $\delta^{18}O_{cc}$ variations exceeding 0.20‰ (as represented by the root of the square sum of the analytical reproducibility and temperature sensitivity) reflect changes in $\delta^{18}O_{gw}$, not temperature (Figure 3c).

This enables one to examine if the maximum possible variability in the groundwater temperature, that is, ±1°C, could contribute to a debated feature of the Devils Hole record, namely that it shows ice-age terminations preceding other archives by ca. 10 ka (Moseley et al., 2016; Winograd et al., 1988, 1992, 2006). Specifically, Termination II occurs at 142 ka in the Devils Hole record (Winograd et al., 1992, 2006) and at 130 ka in the LR04 composite benthic $\delta^{18}O$ record (Lisiecki & Raymo, 2005), which is primarily a proxy of global (deep) seawater temperature and ice volume. The reconstructed Devils Hole $\delta^{18}O_{gw}$ value at 142 ka is −13.55 (±0.20)‰ and at 130 ka is −12.55 (±0.20)‰ (Figure 3c). The observed change in $\delta^{18}O_{gw}$ between these two dates, that is, 1.00‰, significantly exceeds the total uncertainty of 0.40‰ associated with $\delta^{18}O_{gw}$ determinations. Therefore, variations in kinetic fractionation or groundwater temperature cannot be the reason for the particular timing of the ice-age termination shown by the Devils Hole record.

In conclusion, we have demonstrated using dual clumped isotope thermometry that neither variations in temperatures nor variations in reaction kinetics influenced the Devils Hole calcite $\delta^{18}O$ time series to any significant degree. Combined $\Delta_{47}$ and $\Delta_{48}$ measurements enable the characterization of the carbonate precipitation environments for speleothems and other climate archives and, therefore, strengthen the interpretation of the recorded climatic information. Slowly precipitating subaqueous calcites may accurately record changes in groundwater isotope compositions even during glacial-interglacial cycles.

## Data Availability Statement

All study data are deposited at https://zenodo.org/record/4671734

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