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Calibration of the calcite–water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory

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Abstract

The $\delta^{18}O$ of ground water (-13.54 ± 0.05 ‰) and inorganically precipitated Holocene vein calcite ($+14.56 \pm 0.03$ ‰) from Devils Hole cave #2 in southcentral Nevada yield an oxygen isotopic fractionation factor between calcite and water at 33.7 °C of 1.02849 ± 0.00013 ($1000 \ln \alpha_{calcite-water} = 28.09 \pm 0.13$). Using the commonly accepted value of $\partial(\alpha_{calcite-water})/\partial T$ of $-0.00020\ K^{-1}$, this corresponds to a $1000 \ln \alpha_{calcite-water}$ value at 25 °C of 29.80, which differs substantially from the current accepted value of 28.3. Use of previously published oxygen isotopic fractionation factors would yield a calcite precipitation temperature in Devils Hole that is 8 °C lower than the measured ground water temperature. Alternatively, previously published fractionation factors would yield a $\delta^{18}O$ of water, from which the calcite precipitated, that is too negative by 1.5 ‰ using a temperature of 33.7 °C. Several lines of evidence indicate that the geochemical environment of Devils Hole has been remarkably constant for at least 10 ka. Accordingly, a re-evaluation of calcite–water oxygen isotopic fractionation factor may be in order.

Assuming the Devils Hole oxygen isotopic value of $\alpha_{calcite-water}$ represents thermodynamic equilibrium, many marine carbonates are precipitated with a $\delta^{18}O$ value that is too low, apparently due to a kinetic isotopic fractionation that preferentially enriches ^{16}O in the solid carbonate over ^{18}O, feigning oxygen isotopic equilibrium.
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1. INTRODUCTION

For more than 5 decades, the oxygen isotopic fractionation between calcite and water has served as a method to estimate calcite precipitation temperature (McCrea, 1950; Epstein et al., 1953; Tarutani et al., 1969; Kim and O'Neil, 1997). Isotopic fractionation factors can be calculated on theoretical grounds using published vibrational frequencies, measured with laboratory experiments, or determined from measurements of natural systems in geochemical equilibrium. Laboratory calibrations are challenging and have been subject to more uncertainty than desired because it is difficult (and perhaps nearly impossible) to precipitate calcite in oxygen isotopic equilibrium in laboratory experiments. This paper reports on the use of a natural laboratory to calibrate this important isotopic fractionation factor.

Devils Hole Cave (Fig. 1A), in southern Nevada, is a surface collapse into a deep, planar, steeply dipping fault-controlled fissure in Cambrian limestone and dolostone near the center of the 16-km-long, fault-controlled principal discharge area of the Ash Meadows ground water basin (Winograd et al., 1992; Riggs et al., 1994). The approximately 12,000 km^2 Ash Meadows ground water basin is recharged primarily by precipitation in the Spring Mountains (Fig. 1A). Ground water transit times to Devils Hole are at most several thousand years and could be less than a thousand years (Winograd et al., 2006). The Ash Meadows discharge area receives approximately 58,000 $m^3\ d^{-1}$ of ground water supersaturated with respect to calcite (Winograd and Pearson, 1976). The collapse intersects the water table about 15 m below land surface and the open fissure extends at least 130 m deeper. Below water, most of the fissure is lined with a greater than 30-cm-thick-layer of dense mammillary calcite that precipitated continuously from ground water for more than 500 ka (Winograd et al., 1992). Devils

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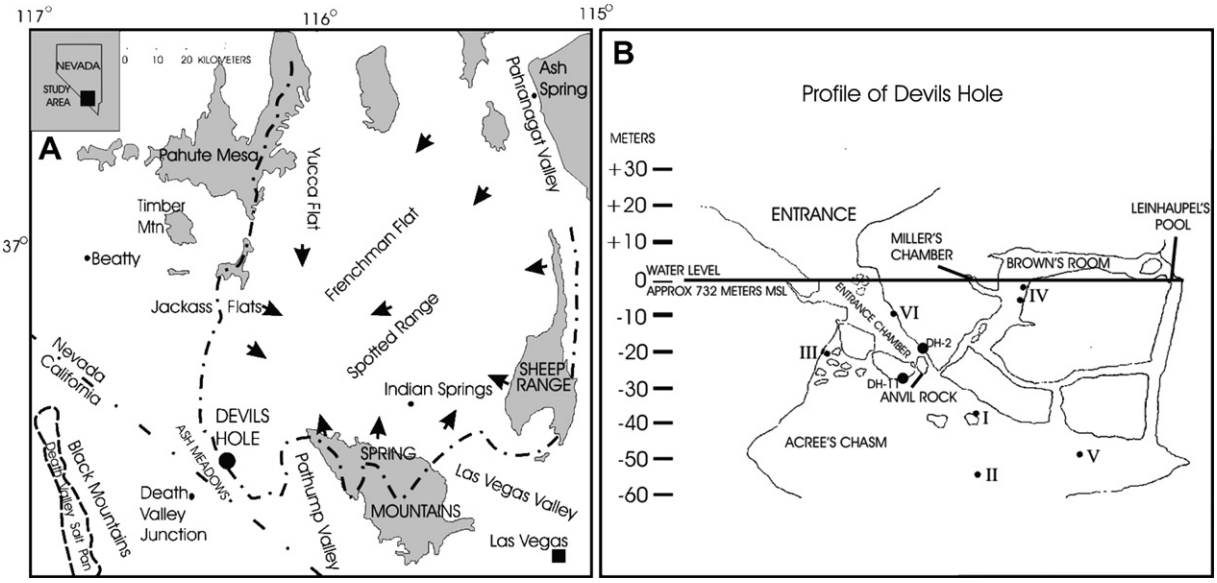

Fig. 1. (A) Map of south-central Nevada, USA, showing location of Devils Hole and recharge areas. Arrows indicate the general direction of ground water flow. Dashed and dotted lines show the approximate boundary of the Ash Meadows ground water basin. From Plummer et al. (2000). (B) Sectional view of the NE–SW striking, steeply dipping fault plane of Devils Hole showing location of Browns Room and of vein calcite samples DH-2 and DH-11. Sites I–VI show locations of crystals in calcite growth studies of Plummer et al. (2000). From Plummer et al. (2000).

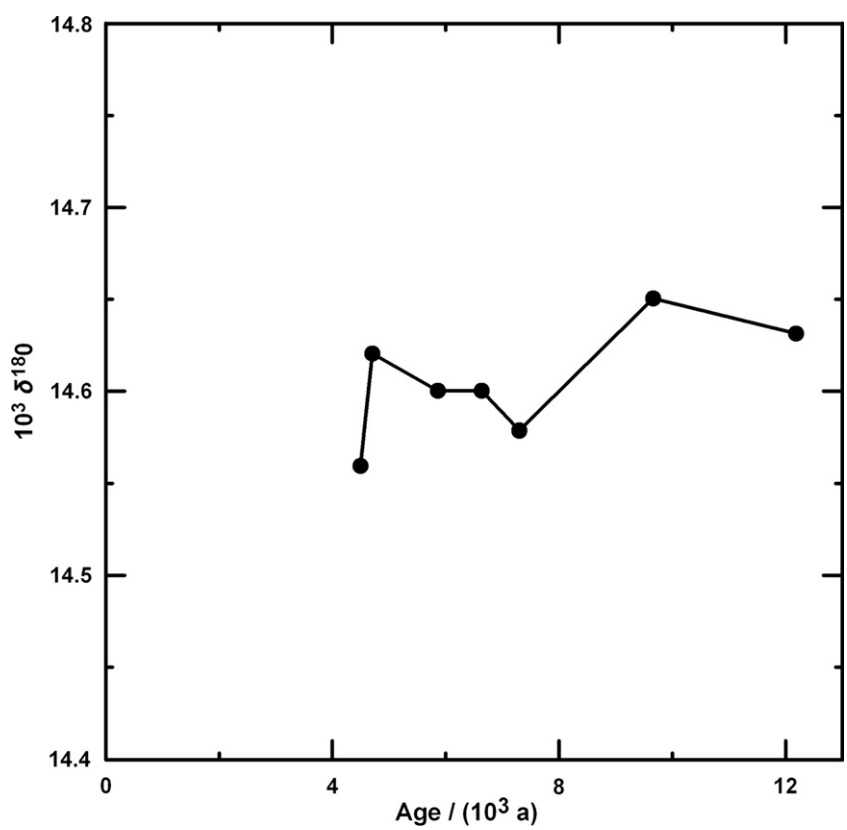

Fig. 2. The Devils Hole $\delta^{18}O$ time series between 13 and 4.5 ka. Black dots, $\delta^{18}O$ analyses of DHC2-8 relative to VSMOW. The accuracy of the $\delta^{18}O$ measurements is ± 0.07 ‰. Modified from Winograd et al. (2006, Fig. 2).

Hole core DH-11 (see Fig. 1B), which yielded this 500,000-a record was recovered from a depth of ~30 m below the water table. The cessation of vein calcite growth ~60,000 years ago was puzzling, given the absence of any hiatuses in the growth of calcite in the preceding ~500,000 a (Winograd et al., 1992) and the likelihood that water has always been supersaturated with respect to calcite (Riggs et al., 1994). It has been speculated that ~60,000 years ago the fissure that comprises Devils Hole opened to the surface and intruded sunlight to the water table, allowing the development of a photosynthetically based aquatic community that included cyanobacterial and algal mats, diatoms, and the endangered Devils Hole pupfish, *Cyprinodon diabolis* (Riggs et al., 1994; Plummer et al., 2000; Winograd et al., 2006). Thereafter, calcite precipitation ceased due to production of a variety of organic molecules that can adsorb onto calcite surfaces and inhibit growth (Plummer et al., 2000). This hypothesis suggested that portions of the cavern up the hydraulic gradient (*i.e.*, upstream in the aquifer) from where DH-11 was collected might yield calcite that grew uninhibited by contaminants. Several divers searched Devils Hole Cave number 2, a similar cave ~200 m north of Devils Hole, for recently precipitated calcite. The first dives in 1994 provided several samples, one of which (DHC2-3) was precipitated from 80,000 to 19,000 years ago, thus, providing 41,000 a of new record (Winograd et al., 2006). Additional dives in 1996 further into the system yielded sample DHC2-8, which grew between 30,000 and ~4500 years ago at a depth of about 60 m below the water table, and overlaps DHC2-3 by 11,000 a (Winograd et al., 2006). It is anticipated that samples collected further up the hydrologic gradient could yield modern calcite. A $\delta^{18}O$ time series for part of the DHC2-8 U-series dated vein calcite samples is given in Fig. 2.

2. EVIDENCE FOR CONSTANCY OF THE GEOCHEMICAL ENVIRONMENT

There are several lines of evidence that suggest that the calcite precipitated in Devils Hole from ground water of known $\delta^{18}O$ and temperature is in isotopic equilibrium or as close to equilibrium as one is likely to find in a natural system. These lines of evidence include:

1. The temperature of Devils Hole ground water has remained constant over the short term and over the long term (hundreds of thousands of years). Periodic measurements of water chemistry and temperature indicate near constant conditions in the cavern since the early 1930s (Winograd and Pearson, 1976). Such uniformity is not unexpected at the discharge end of an unstressed (by pumping) ground water basin of this size. Plummer et al. (2000) measured 33.7 ± 0.2 °C in the main chamber of Devils Hole at depths of 5, 25, and 37.5 m below water level with an armored Hg thermometer readable to 0.05 °C in March 1985 (Table 1). This is in good agreement with temperature measurements in November 1954 of 33.9 °C (2 m below the surface), 34.0 °C (15 m below the surface), and 34.0 °C (29 m below the surface), and measurements in April 1961 of 34.0 °C (1.3 m below the surface) and 34.3 °C (27 m below the surface) (Hoffman, 1988). For the period 1930–1947, Miller (1948) reports 8 readings ranging from 32.8 to 33.9 °C. Lastly, Dudley and Larson (1976) report 33.5 °C for a December 1966 measurement.
   Ground water temperature also has been relatively constant on long time scales, presumably due to the large size of the Ash Meadows ground water basin. Winograd et al. (1992, reference note #9) compared the $\delta^{18}O$ of vein calcite with the $\delta^{2}H$ of fluid inclusions in the same calcite samples precipitated during the penultimate full glacial and peak interglacial at approximately 160 and 130 ka, respectively, because one might expect maximum temperature differences between full glacial and peak interglacial times. The $\delta^{2}H$ of fluid inclusions was determined by (i) soaking each calcite vein sample in water with a $\delta^{2}H$ value of approximately −103 ‰ to buffer the isotopic composition of any surface water, (ii) removing surface water under vacuum for 16 h at 150 °C in a stainless steel tube, (iii) crushing the sample in the stainless steel tube to expose pore fluid, and (iv) collecting pore-fluid water liberated from the sample while heating at 250 °C for a minimum of 3 h. The difference in the $\delta^{2}H$ values of water trapped during the penultimate full glacial and peak of the last interglacial is 14 ‰ (2-σ uncertainty of ±2 ‰) and the difference in oxygen-isotope ratios is 2.1 ‰ (2-σ uncertainty of ±0.14 ‰). Assuming a relationship of 8 between variation in $\delta^{2}H$ and $\delta^{18}O$ values, the change in oxygen-isotope ratios in the calcite between 160 and 130 ka is fully attributable to change in the $\delta^{18}O$ of ground water, and no change in water temperature is indicated. Use of the value of 8 is in accord with the local meteoric water line of $\delta^{2}H = 7.8\ \delta^{18}O + 7.2$ ($R = 0.99$), determined with spring waters, snow, snowmelt, and rain (Winograd et al., 1998). Over shorter periods (seasons, years, decades, and centuries) no significant variation in temperature is expected because of the large size of the Ash Meadows ground water basin.
   There are no measurable $\delta^{18}O$ differences in calcite precipitated contemporaneously at the sites from which vein calcite samples have been collected, which span a vertical distance of 60 m and a horizontal distance of ~200 m. As previously mentioned, $\delta^{18}O$ profiles of three overlapping (in time) samples of vein calcite, a ~568-ka-long time series, have been extracted from DH-2 (Fig. 1B) and DH-11 (Fig. 1B) in the main chamber of Devils Hole (Winograd et al., 1992; Coplen et al., 1994) and DHC2-3 and DHC2-8 (Winograd et al., 2006) in Devils Hole Cave 2, 200 m distant from Devils Hole. The $\delta^{18}O$ profiles in each sample agree to within ±0.1 ‰, indicating that temperature differences between sampling sites are less than 0.5 °C because the temperature coefficient of the calcite–water oxygen isotopic fractionation factor is $-0.00020\ K^{-1}$ (Epstein et al., 1953) and because the $\delta^{18}O$ of water throughout Devils Hole is constant (see below).
2. Had vein calcite precipitated in Devils Hole during the last 4.5 ka, its $\delta^{18}O$ variation would have been approximately ±0.1 ‰. This assertion derives from the near

Table 1
Chemical composition of groundwater collected March 1985 from Devils Hole, Nevada (Plummer et al., 2000, Table I)

Parameter	Site I	Site III	Site IV
Depth (m)	37.5	25	5
Temperature (°C)	33.7	33.7	33.7
pH	7.39	7.37	7.43
Ca (mg/L)	49.5	49.6	49.4
Mg (mg/L)	22	22	22
Na (mg/L)	67	67	67
K (mg/L)	7.9	8.0	7.9
Cl (mg/L)	21	21	22
SO_4 (mg/L)	82	83	83
Alkalinity (mg/L, HCO_3)	305.4	305.5	305.3
F (mg/L)	1.4	1.5	1.5
$NO_2 + NO_3$ (N) (mg/L)	0.15	0.14	0.15
NH_4 (N) (mg/L)	0.009	0.015	0.02
P, ortho (P) (mg/L)	<0.01	<0.01	<0.01
DOC (C) (mg/L)	0.2	0.2	0.2
Ba (μg/L)	87	88	88
Beryllium (μg/L)	<0.5	<0.5	<0.5
B (μg/L)	350	350	350
Br (mg/L)	0.14	0.15	0.15
Cd (μg/L)	1	<1	<1
Co (μg/L)	<3	<3	<3
Cu (μg/L)	<10	<10	<10
Fe (μg/L)	<3	<3	<3
Pb (μg/L)	<10	<10	<10
Li (μg/L)	84	84	83
Mn (μg/L)	4	4	4
Mo (μg/L)	<10	10	<10
Silica (mg/L)	23	23	23
Specific conductance (μS/cm)	682	684	685
Sr (μg/L)	890	890	890
V (μg/L)	<6	<6	<6
Zn (μg/L)	9	8	8
Charge balance (%)	0.3	0.1	−0.1
TDIC (mmol/kg H_2O, calc.)	5.35	5.37	5.32
SI (calcite)	0.18	0.16	0.21
log p_{CO_2}	−1.87	−1.85	−1.91

synchronous variations between the Devils Hole $\delta^{18}O$ vein calcite record and sea surface temperature (SST) in marine cores off California as discussed in detail by Winograd et al. (2006) and Herbert et al. (2001). For the period between 160,000 and 4500 a, during which the $\delta^{18}O$ of Devils Hole vein calcite varied by as much as 2.5 ‰ over glacial-interglacial time scales (Fig. 2 of Winograd et al., 2006), between 78% and 83% of the variation in SST is shared with the Devils Hole $\delta^{18}O$ vein calcite record (Fig. 6 of Winograd et al., 2006, and related text), and thus with the $\delta^{18}O$ of Devils Hole water. Between 17 and 4.5 ka when the DHC2-8 record terminates, its $\delta^{18}O$ variation was less than 0.2 ‰. The $\delta^{18}O$ of calcite vein sample DHC2-8 does not exceed the bounds of $+14.56 \pm 0.1$ ‰ between 12 and 4.5 ka (Fig. 2); thus, the $\delta^{18}O$ of Devils Hole water should also have been constant within ±0.1 ‰ during this period. Between 4.5 and 0 ka SST has been relatively constant (Fig. 3 of Herbert et al., 2001; Figs. 3 and 4 of Winograd et al., 2006). Likewise, Greenland ice cores show that the $\delta^{18}O$ record between 10 and 0 ka is constant and stable (Figs. 3 and 7 of Johnson et al., 2001). Therefore, had poisoning of core DHC2-8 for calcite precipitation not occurred ~4.5 ka, a strong case can be made that the $\delta^{18}O$ of vein calcite precipitated between 4.5 and 0 ka would lie within the same bounds ($+14.56 \pm 0.1$ ‰).

3. Only calcite is present in Devils Hole vein material collected below the water table. Petrographic and X-ray mineralogy studies indicate that no aragonite or any other minerals have been precipitated with the vein calcite during the past 568 ka (Winograd et al., 1992; Kolesar and Riggs, 2004; Winograd et al., 2006). Thin section examination shows no evidence of dissolution, recrystallization, or hiatuses within any of the three profiles comprising the ~568-ka-long time series, providing additional evidence that the water has always been supersaturated.
4. It is thought that isotopic equilibrium is promoted by slow calcite growth rates (Tarutani et al., 1969; Kim and O'Neil, 1997). During the past 80–4.5 ka, the best-dated part of the record, the calcite precipitation rate as determined from U-series dated samples, has varied from 0.1 to 0.8 μm a^{-1} (Winograd et al., 2006). These rates are one to several orders of magnitude slower than growth rates of speleothems or of travertines, which range from 10 to 1000 μm a^{-1} (McDermott, 2004), and probably reflect the slight supersaturation of Devil Hole ground waters (see Table 1). The modern saturation index of calcite (the ratio of the calcium carbonate apparent ionic product to the apparent solubility product of calcite) in Devils Hole ranges from 0.16 to 0.21 (Table 1). Plummer et al. (2000) found that crystals of Iceland spar placed in Devils Hole grew initially at a rate of 0.22 μm a^{-1}, but slowed or ceased growing following prolonged contact with Devils Hole ground water, apparently due to poisoning of the calcite surface (Plummer et al., 2000) as discussed above.
5. Coplen et al. (1994) demonstrated that calcite is precipitated in Devils Hole in carbon isotopic equilibrium, and Winograd et al. (1992) and Coplen et al. (1994) examined several lines of evidence and could find no basis for precipitation of vein calcite in oxygen isotopic disequilibrium.

Briefly, taken together the various lines of evidence outlined above suggest that Devils Hole is well suited as a natural laboratory to calibrate the calcite–water oxygen-isotope geothermometer.

3. ANALYTICAL METHODS

The distribution of the amounts of isotopes between two phases is given by the isotopic fractionation factor α. For the calcite–water oxygen isotopic fraction factor, this is given by

$$\alpha_{\text{calcite–water}} = \frac{n_{\text{calcite}}(^{18}\text{O})/n_{\text{calcite}}(^{16}\text{O})}{n_{\text{water}}(^{18}\text{O})/n_{\text{water}}(^{16}\text{O})} \quad (1)$$

where $n_{\text{calcite}}(^{18}\text{O})$ and $n_{\text{calcite}}(^{16}\text{O})$ are, respectively, the amounts of ^{18}O and ^{16}O in calcite in units of moles, and similarly for those parameters in water. Differences in

measured isotope-amount ratios of stable oxygen isotopes ($^{18}O/^{16}O$) in a sample relative to that in VSMOW reference water are reported as a delta value. Thus, for a sample A:

$$\delta^{18}O = \frac{n_A(^{18}O)/n_A(^{16}O) - n_{VSMOW}(^{18}O)/n_{VSMOW}(^{16}O)}{n_{VSMOW}(^{18}O)/n_{VSMOW}(^{16}O)} \quad (2)$$

In the same manner, $\delta^{13}C$ values are reported relative to the VPDB scale by anchoring this scale with assignment of $\delta^{13}C$ of NBS 19 calcite as +1.95 ‰.

Water was analyzed for $\delta^{18}O$ using the method of Epstein and Mayeda (1953). Results are expressed on a scale normalized such that the $\delta^{18}O$ of SLAP reference water is −55.5 ‰ (Gonfiantini, 1978). CO_2 was liberated from carbonates for $\delta^{18}O$ and $\delta^{13}C$ analysis with 100% H_3PO_4 using the method of McCrea (1950). CO_2 was analyzed on a double-focusing, double-collecting isotope-ratio mass spectrometer (Coplen, 1973). The $\delta^{18}O$ values of carbonates were calculated using a CO_2–H_2O oxygen isotopic fractionation factor of 1.04120 (O'Neil et al., 1975) and a CO_2–calcite oxygen isotopic acid fractionation factor of 1.01025 at 25 °C (Friedman and O'Neil, 1977). Because the 2-σ standard deviation (0.00030) of the CO_2–calcite oxygen isotopic acid fractionation factor determination of Kim and O'Neil (1997) of 1.01050 encompasses the value of 1.01025, the later was used in this report. Had the value of 1.01050 been used, the $\delta^{18}O$ values of all carbonates analyzed herein would be lower by 0.25 ‰. It is critical that $\delta^{18}O$ values of carbonates be reported on the same normalized scale as that used for water (Coplen, 1996) and that is done herein.

4. RESULTS

The $\delta^{18}O$ of calcite from the outer 0.1-mm surface of sample DHC2-8, whose outer surface has an age of ~4.5 ka (Winograd et al., 2006), is +14.56 ± 0.03 ‰ (Table 2) and does not exceed the bounds of +14.56 ± 0.1 ‰ between 12 and 4.5 ka (Fig. 2). The internationally distributed reference materials NBS 18 and NBS 19 were analyzed simultaneously with DHC2-8 and their $\delta^{18}O$ values are +7.20 ± 0.02 ‰ and +28.65 ± 0.06 ‰, respectively. These values are in excellent agreement with the values of +7.20 ± 0.03 ‰ and +28.65 ± 0.02 ‰, reported by Coplen et al. (1983).

Table 2
$\delta^{18}O$ values of waters and carbonates in this study[a]

Name	Description	$10^3\ \delta^{18}O$	n
VSMOW	Water	0 ± 0.05	12
DH[b]	Water	−13.54 ± 0.05	6
SLAP	Water	−55.5 ± 0.04	12
NBS 19	Calcite	+28.65 ± 0.06	6
DHC2-8	Calcite	+14.56 ± 0.03	8
NBS 18	Calcium carbonate	+7.20 ± 0.02	6

[a] $\delta^{18}O$ values are expressed relative to VSMOW and normalized to SLAP ≡ −55.5 ‰. Reported uncertainties are 1σ. The $\delta^{18}O$ values of carbonates were calculated using a CO_2–H_2O oxygen isotopic fractionation factor of 1.04120 (O'Neil et al., 1975) and a CO_2–calcite oxygen isotopic acid fractionation factor of 1.01025 (Friedman and O'Neil, 1977), both at 25 °C.

[b] DH is a single water sample that was analyzed 6 times. Neither temperature nor water chemistry varies with depth (Plummer et al., 2000, Table 1 herein); thus, there is no reason to expect $\delta^{18}O$ to vary.

The $\delta^{18}O$ of water (collected November 20, 2000) from Devils Hole is −13.54 ± 0.05 ‰. This agrees well with the value of −13.6 ± 0.2 ‰ of a sample collected November 1973 (Winograd and Pearson, 1976). The oxygen isotopic fractionation between DHC2-8 calcite and Devils Hole water is (1 + 0.01456)/(1 − 0.01354), which equals 1.02849 ± 0.00013. The uncertainty is the square root of the square of the analytical uncertainty (0.00008) and the square of the variability in $\delta^{18}O$ of calcite between 12 and 4.5 ka (0.00010). Commonly, these values are reported as 1000 ln α, which is 28.09 ± 0.13.

5. DISCUSSION

5.1. Comparison with experimental studies

There have been several experimental studies to determine the oxygen isotopic fractionation between inorganically precipitated calcite and water (O'Neil et al., 1969; Tarutani et al., 1969; Kim and O'Neil, 1997; Jiménez-López et al., 2001, 2004; Zhou and Zheng, 2003, 2005). Results from these studies are compared with the value determined from Devils Hole in Fig. 3. The 1000 ln α values of Tarutani et al. shown in Fig. 3 have been increased by 0.28 as recommended by Kim and O'Neil (1997) to be in accord with Friedman and O'Neil (1977). The 1000 ln α values of Kim and O'Neil (1997) shown in Fig. 3 have been increased by 0.25 to be consistent with use of a CO_2–calcite oxygen isotopic acid fractionation factor of 1.01025 (Friedman and O'Neil, 1977). The data of Zhou and Zheng (2003, 2005) is not presented in Fig. 3 or discussed further because their method lacks documentation (Horita and Clayton, 2007).

It is apparent on Fig. 3 that the 1000 ln α value of 28.09 from Devils Hole samples would yield a temperature of about 26 °C using the α of Kim and O'Neil (1997), which is about 8 °C lower than measured temperature. Individual measurements of $\alpha_{calcite-water}$ of both Tarutani et al. (1969) and Kim and O'Neil (1997) span a relatively large range (Fig. 3). To arrive at their published isotopic fraction factors, authors of both papers selected their lowest values of α, which were produced by experiments with the lowest initial concentrations of dissolved carbonate (initial calcium concentrations of approximately 5 mM). Jiménez-López et al. (2001) performed a single 1440-min experiment in which 1000 ln α values determined during the experiment ranged between 26.62 and 28.30, suggesting that oxygen isotopic equilibrium was not achieved. None of these published laboratory-determined oxygen isotopic fractionation factors agree with that determined from Holocene Devils Hole calcite and water.

The reason for the substantial difference between that found in previous laboratory determinations and that determined in this study is unclear, but it may be related to two different reasons. First, the authors of these papers may have failed to report $\delta^{18}O$ values of solid carbonates on a scale normalized such that the $\delta^{18}O$ of SLAP reference water is −55.5 ‰ exactly. The recommendation in 1978 by

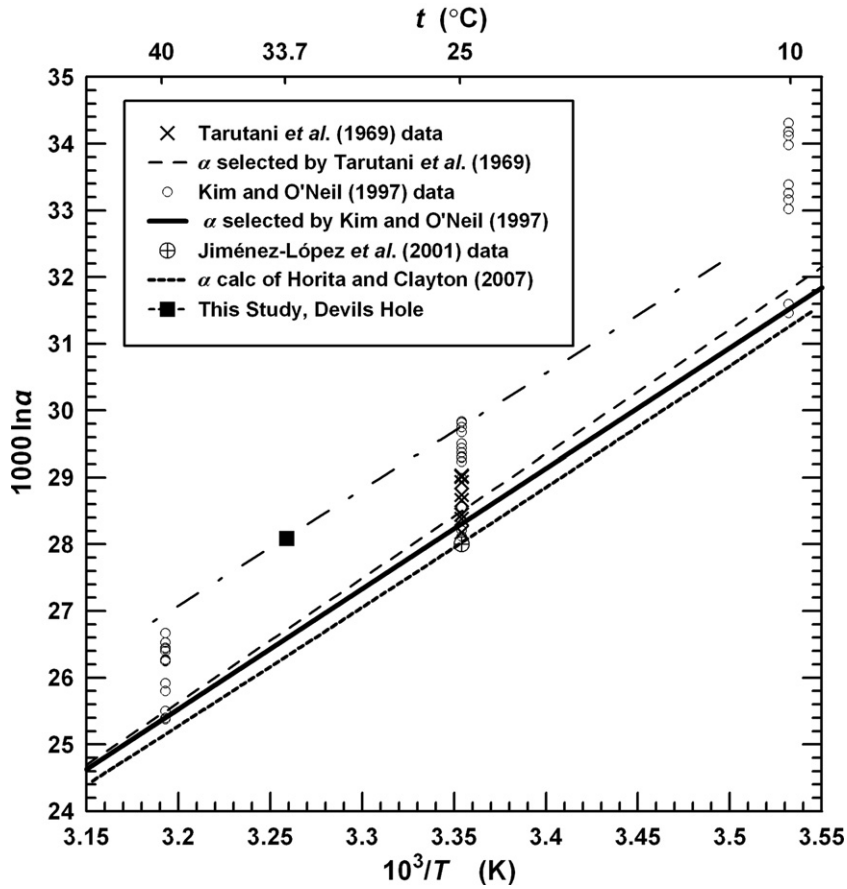

Fig. 3. Comparison of calcite–water oxygen isotopic fractionation factors. The size of the solid square reflects an uncertainty value ($1 \times u_C$) estimated for the oxygen isotopic fractionation factor in this study. The dotted line through the Devils Hole point was constructed with a value of $\partial(\alpha_{calcite-water})/\partial T$ of $-0.00020\ K^{-1}$.

Gonfiantini (1978) was to normalize water samples, but not oxygen-bearing solids, to a scale on which $\delta^{18}O$ of SLAP reference water is −55.5 ‰. Thus, some authors normalize $\delta^{18}O$ values of water, but not $\delta^{18}O$ values of carbonates. As pointed out by Gonfiantini (1984), failing to normalize the $\delta^{18}O$ of solids on a scale with two anchors generates incorrect values of α. Information that would allow the reader to determine exactly how or if normalization of carbonates was carried out is missing from all three experimental studies. Had $\delta^{18}O$ values of international isotopic reference materials NBS 18 and NBS 19 that were interspersed among unknowns been provided in the latter investigations, the reader would be able to evaluate $\delta^{18}O$ scale normalization. This could not have been done in the earliest study because these materials did not exist in 1969.

Second, calcite may have been precipitated in oxygen isotopic disequilibrium with water in laboratory experiments. The initial Ca concentration in the Tarutani et al. (1969) experiments ranged between 182 and 420 mg/L and that of the Kim and O'Neil (1997) experiments ranged between 200 and 1000 mg/L. These Ca concentrations are substantially greater than the value of 49.5 mg/L found in Devils Hole at a depth of 37.5 m below the water table, where the calcite saturation index is 0.18 (Plummer et al., 2000); yet, the value of α from Devils Hole samples is higher than that determined in either experimental study. Both Tarutani et al. (1969) and Kim and O'Neil (1997) found a substantial correlation of oxygen isotopic fractionation with initial Ca concentration, with higher Ca concentrations giving rise to larger isotopic fractionation. Kim and O'Neil (1997) state "The fractionation factors measured for solutions with different initial concentrations differed by as much as 2–3 ‰ at a given temperature. Clearly there is one and only one equilibrium fractionation at any temperature, so most of the carbonates precipitating from these solutions of varying concentration were forming out of oxygen-isotope equilibrium with the water. Only limited criteria were available to use in selecting which direction of change (*i.e.*, larger or smaller fractionations), if any, was in the direction toward equilibrium".

The fact that both Tarutani et al. (1969) and Kim and O'Neil (1997) selected their lowest values of α, which were produced by experiments with the lowest initial concentrations of dissolved carbonate, may be problematic. A reviewer of this manuscript (Prof. T. Vennemann, personal communication, 2007) stated, "For example, there is no *a priori* reason why lower Ca concentrations should give better estimates of the calcite–water oxygen-isotope fractionations compared to higher Ca concentrations. Kinetic considerations may suggest preferential incorporation of

the isotopically light species (*e.g.*, CO_3^{2-}) during rapid precipitation, which is in contrast to the argumentation given by Tartuani et al. and Kim and O'Neil, but would support the present conclusions, for example". In Fig. 3, a dotted line with a slope of $\partial(\alpha_{calcite-water})/\partial T$ of $-0.00020\ K^{-1}$ has been drawn through the Devils Hole point, and the equation,

$$1000 \ln \alpha_{calcite-water} = 17.4(1000/T) - 28.6 \quad (3)$$

gives a satisfactory fit between 13 and 40 °C. Note that data points from the Kim and O'Neil (1997) experimental study either bound this dotted line or are within 0.2 ‰ of its extension from 13 to 10 °C.

5.2. Comparison with theoretical calculations

The equilibrium oxygen isotopic fractionation factor between calcite and water between 0 and 100 °C has been determined based largely on statistical–mechanical calculations by Horita and Clayton (2007) and is shown in Fig. 3. Their calculated curve lies below nearly all of the experimental measurements and substantially below the Devils Hole result. They suggest that their calculated results can be reconciled if one adopts a value of 1.0407 instead of 1.0412 for the oxygen isotopic fractionation between gaseous CO_2 and water. The problem with this hypothesis is that it is more likely that the value of 1.0412 is too low rather than too high. The value of 1.0412 was determined in concert with a value of −55.5 ‰ for SLAP reference water relative to VSMOW reference water (see Fig. 1 of Hut, 1987). This consensus value for SLAP reference water is a mean of measurements from 35 laboratories (Gonfiantini, 1978), and it is now known that it should be between −55.7 ‰ and −56.2 ‰ (Verkouteren and Klinedinst, 2004). Increasing the span between VSMOW and SLAP reference water is expected to cause an increase in the oxygen isotopic fractionation between gaseous CO_2 and water (Gonfiantini, 1984), rather than a decrease that is needed to reconcile the calculations of Horita and Clayton (2007).

Horita and Clayton (2007) provide an equation for the oxygen isotopic fractionation between calcite and water and they provide no numerical value for uncertainty. With all of the assumptions listed by Horita and Clayton to determine their algorithm, could it be that the uncertainty bounds in $1000 \ln \alpha$ values are ±0.5, or could they be as high as ±2? If the uncertainty of $1000 \ln \alpha$ is ±2, the calculated algorithm of Horita and Clayton is in agreement with the Devils Hole oxygen isotopic fractionation factor (Fig. 3).

5.3. $\delta^{13}C$ comparisons

DHC2-8 vein calcite is in carbon isotopic equilibrium with dissolved inorganic carbon (DIC) in Devils Hole. The $\delta^{13}C$ of DIC is -4.8 ± 0.2 ‰ (Coplen et al., 1994). With a pH of 7.39, the fractions of HCO_3^- and $CO_{2(aq)}$ are 0.936 and 0.064, respectively. Using the carbon isotopic fractionation factors of Vogel et al. (1970) and Mook et al. (1974), the $\delta^{13}C$ of HCO_3^- and $CO_{2(aq)}$ are −4.3 ‰ and −12.4 ‰, respectively. Using the carbon isotopic fractionation factors of Bottinga (1968) and Mook et al. (1974), the $\delta^{13}C$ of precipitating calcite should be -2.1 ± 0.2 ‰. This is in excellent agreement with the measured value of DHC2-8 of -2.05 ± 0.05 ‰ ($n = 8$).

5.4. Browns room flashbulb

Coplen et al. (1994) reported that modern calcite was forming on a flashbulb found floating in Browns Room (Fig. 1B), a cave extending 9 m above the water table in Devils Hole. Calcite was precipitated at 33.7 °C (Hoffman, 1988), presumably by loss of aqueous CO_2 ($\log p_{CO_2} =\sim -1.9$, Table 1). No measurable change in oxygen isotopic composition due to evaporation of water is likely because the relative humidity in Browns Room is 100%.

About 1 mm of calcite was precipitated on the flashbulb in an estimated 3 to 4 decades, which gives a precipitation rate of about 30 μm a^{-1}. This is one or two orders of magnitude greater than the growth rate of DHC2-8 during the past 80 ka (0.1–0.8 μm a^{-1}; Winograd et al., 2006; Fig. 2 herein). The mode and rate of growth on the flashbulb is probably similar to that of speleothems, and the calcite will not be in oxygen and carbon isotopic equilibrium if loss of CO_2 is too rapid. In such a case, calcite can be formed in isotopic disequilibrium and can be enriched in ^{18}O and ^{13}C according to Hendy (1971). The $\delta^{13}C$ of the calcite on the flashbulb is −1.75 ‰, which is 0.3 ‰ more positive, than that of core DHC2-8 (−2.05 ‰); thus, the flashbulb calcite appears not to be in isotopic equilibrium with Devils Hole water. The $\delta^{18}O$ of the flashbulb calcite should not be used to quantify the value of $\alpha_{calcite-water}$ (Hendy, 1971). Nevertheless, it is useful to compare the $\delta^{18}O$ of the flashbulb calcite with that of core DHC2-8. The $\delta^{18}O$ of the calcite on the flashbulb is +14.2 ‰, which is similar to the value of +14.56 ‰ of DHC2-8. Based on the work of Hendy (1971), one might have expected the flashbulb calcite to be enriched in ^{18}O relative to that of core DHC2-8. However, the lower $\delta^{18}O$ value of the flashbulb calcite is in accord with preferential incorporation of the ^{16}O-enriched species of CO_3^2 during rapid non-oxygen isotopic equilibrium precipitation as suggested by one of the reviewers (Prof. T. Vennemann; see discussion above, personal communication, 2007).

5.5. Marine carbonate precipitation

Although oxygen isotopic fractionation between calcite and water is widely used to investigate the temperature and fluid composition under the assumption that isotopic equilibrium is maintained (McCrea, 1950; Epstein et al., 1953), there is serious concern that neither thermodynamic or oxygen isotopic equilibrium is maintained during marine carbonate precipitation for a number of reasons. In discussing coprecipitation reactions and solid solutions of carbonate minerals, Morse and Mackenzie (Chapter 3, 1990) conclude, "In summary, there is no reason to expect that partition coefficients in calcite should not be precipitation rate dependent". Additionally, biogenic carbonates are distinctly different in their chemical and physical properties from well-crystallized, chemically homogeneous, synthetic

Table 3
The $\delta^{18}O$ values of calcite precipitated at 33.7 °C from sea water with a $\delta^{18}O$ value of 0 ‰

Source	Description[a,b]	$10^3\ \delta^{18}O$
Sharp (2007) Eq. (6.5)[c]	$t = 15.75 - 4300(\delta_c - \delta_w) + 140{,}000(\delta_c - \delta_w)^2$	−3.72
Mulitza et al. (2003)[c]	$t = 14.32 - 4280(\delta_c - \delta_w) + 70{,}000(\delta_c - \delta_w)^2$	−4.23
O'Neil et al. (1969)	$1000 \ln \alpha_{calcite-water} = (2.78 \times 10^6)/T^2 - 2.89$	−3.81
Kim and O'Neil (1997)	$1000 \ln \alpha_{calcite-water} = 18.03(10^3\ T^{-1}) - 32.42$	−4.10
This study	$\alpha_{calcite-water} = 1.02849$	−2.35

[a] $\delta_c = \delta^{18}O$ of calcite relative to VPDB using the conversion relationship $1 + \delta^{18}O_{x-VPDB} = 0.97001(1 + \delta^{18}O_{x-VSMOW})$ (Coplen et al., 2001).
[b] $\delta_w = \delta^{18}O$ of water relative to VSMOW = 0 ‰.
[c] Equation has been reformulated to be in accord with the definition of delta herein (Eq. (2)), which is a quantity equation.

samples of similar bulk composition (Morse and Mackenzie, 1990); therefore, they should not be expected to have the same oxygen isotopic fractionation factors. Precipitation of carbonates is complicated. During laboratory precipitation experiments of calcite from intermediate ionic solution at 25 °C, monohydrocalcite precipitated initially at a solution saturation slightly greater than 1 (Jiménez-López et al., 2001; Jiménez-López et al., 2004). Subsequently, calcite crystallized at a solution saturation of ~14.4 and was accompanied by dissolution of monohydrocalcite at a rate that exceeded calcite precipitation, producing anomalous behavior in the chemical and isotopic composition of the system. Plummer et al. (1992) explain that such phenomena is due to formation of a monolayer solid solution on the mineral surface with an ion activity product intermediate between that of the pure endmembers. Dickson (1991) shows that inorganic calcite can have substantial spatial variations in oxygen isotopic composition (~0.9 ‰) on different crystal faces in the same growth zone. Additionally, many biogenically precipitated carbonates are not precipitated in oxygen isotopic equilibrium, but in oxygen isotopic disequilibrium due to so called "vital effects" that are controlled by metabolic processes. If aragonite is precipitated instead of calcite, it may recrystallize during diagenesis to calcite, and its oxygen isotopic composition may or may not be preserved (Lowenstam, 1961). Nevertheless, it is instructive to compare the Devils Hole $\alpha_{calcite-water}$ value with previous values.

The $\delta^{18}O$ values of calcite precipitated at 33.7 °C from sea water with a $\delta^{18}O$ value of 0 ‰ using five relationships are shown in Table 3. The Devils Hole result (−2.35 ‰) agrees most closely with the $\delta^{18}O$ (−3.72 ‰) determined by the relationship of Sharp (2007), which is a rewritten version of the Epstein et al. (1953) paleotemperature equation. The algorithm of Mulitza et al. (2003) was developed from South Atlantic foraminifera calcite. The $\delta^{18}O$ values using the O'Neil et al. (1969) and the Kim and O'Neil (1997) relationships are listed in Table 3 for completeness.

As compared to other investigations, the author suggests that the closest approach to true thermodynamic equilibrium in the calcite–water oxygen-isotope system is achieved at Devils Hole because the calcite grow rate is very low and because the geochemical environment is stable. If kinetic isotopic fractionation promotes enrichment of ^{16}O relative to ^{18}O in the carbonate, then the carbonate specimens analyzed by Kim and O'Neil (1997) and Mulitza et al. (2003) that lead to the most negative $\delta^{18}O$ values in column 3 of Table 3 appear to be the farthest from thermodynamic equilibrium. The author suggests that the carbonate-water oxygen isotopic temperature scale of McCrea (1950) and Epstein et al. (1953) works as satisfactorily as it does because many marine carbonates are precipitated with an approximately constant oxygen isotopic kinetic fractionation that feigns oxygen isotopic equilibrium—it might be called pseudo-equilibrium precipitation. Under this scenario, at 33.7 °C the difference between kinetically precipitated calcite and equilibrium precipitated calcite is ~1.4 ‰.

6. CONCLUSIONS

Calculation of the temperature of calcite precipitation in Devils Hole using previously published isotopic fractionation factors gives a temperature that is too low by 8 °C. Alternatively, calculation with previously published isotopic fractionation factors of the $\delta^{18}O$ of water that precipitated vein calcite in Devils Hole cave #2 yields a value that is too low by 1.5 ‰. A re-evaluation of carbonate-water oxygen isotopic fractionation factors may be in order in light of these results from the Devils Hole natural laboratory.

If the Devils Hole oxygen isotopic value of $\alpha_{calcite-water}$ represents thermodynamic equilibrium, many marine carbonates are precipitated with a $\delta^{18}O$ value that is too negative, presumably due to a kinetic isotopic fractionation factor that preferentially enriches ^{16}O in the solid carbonate over ^{18}O, simulating oxygen isotopic equilibrium.

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