Earth and Planetary Science Letters 400 (2014) 251–260

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

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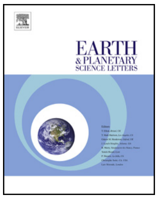

# Devils Hole paleotemperatures and implications for oxygen isotope equilibrium fractionation

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ARTICLE INFO

*Article history:*
Received 24 July 2013
Received in revised form 9 May 2014
Accepted 26 May 2014
Available online 12 June 2014
Editor: G.M. Henderson

*Keywords:*
oxygen isotopes
clumped isotopes
paleothermometry
equilibrium fractionation
degassing effects
growth rate

## ABSTRACT

Subaqueous calcite in Devils Hole, Nevada, was growing continuously from slightly super-saturated groundwater, providing a 570 kyr-long $\delta^{18}O$ paleoclimate record. Due to its very slow growth it has been assumed to have grown under conditions of isotopic equilibrium. However, its Holocene $\delta^{18}O$ value is 1.5‰ higher than predicted by laboratory-precipitation-based oxygen isotope thermometer calibrations. The suggestion that Devils Hole calcite anchors the isotope thermometer to more $^{18}O$-enriched values has stirred a debate as to which paleothermometer calibration is relevant for paleoclimate and casts doubt on the validity of $\delta^{18}O$-based paleotemperatures.

We used clumped isotopes to test the assumptions of the Devils Hole alternative $^{18}O$-thermometer. Carbonate clumped isotopes are a temperature proxy that measures the abundance of $^{13}C$–$^{18}O$ bonds in $CaCO_3$. This proxy is independent of the water composition and therefore gives independent estimates of temperatures when calcite forms at thermodynamic and isotopic equilibrium. We find that Devils Hole water paleotemperatures were constant at $30.6 \pm 2.6\,°C$ between 27 and 180 ka, similarly to the modern groundwater temperature of 32.8–34.3 °C. The proximity of the Devils Hole clumped isotope data to values expected based on modern groundwater temperatures supports the notion that Devils Hole calcite grew under equilibrium conditions. Therefore, the commonly used laboratory-based $\delta^{18}O$-temperature calibrations should be reconsidered.

The constant water temperature over the glacial–interglacial cycles indicates that the long Devils Hole $\delta^{18}O$ record reflects only variations in the groundwater $\delta^{18}O$ values and as such, represents a valuable archive of paleoclimate and isotope paleohydrology.

## 1. Introduction

The equilibrium fractionation of oxygen isotopes during carbonate formation yields unique insights into past environmental conditions and can provide information about past temperatures and hydrological parameters. This classical method has been used for paleotemperature reconstructions at different time scales and using a variety of carbonate materials. It has been applied to biogenic and abiogenic samples to determine, for instance, the Phanerozoic sea-surface temperature evolution (e.g., Veizer et al., 2000), details of the Paleocene–Eocene thermal maximum (Zachos et al., 2003), Quaternary sea-surface temperatures (e.g., Emiliani, 1955; Shackleton and Opdyke, 1973; Emiliani and Shackleton, 1974), and the continental temperature evolution during the last glacial cycle and the Holocene (e.g., Duplessy et al., 1970; Dorale et al., 1992).

A unique and hotly debated continental paleoclimate record was derived from mammillary calcite that was retrieved from two neighboring caves in the desert of Nevada: Devils Hole (Winograd et al., 1992; Coplen et al., 1994) and Devils Hole #2 (Winograd et al., 2006). The two sites represent the same hydrological and chemical system as they both intersect the same aquifer and therefore will be simply referred to as the Devils Hole system. Devils Hole is not a karstic cave system as dissolution played almost no role in creating the voids, which are of tectonic, extensional origin (Riggs et al., 1994).

The isotopic record of Devils Hole calcite covers the Quaternary from about 570 ka to the mid Holocene (Winograd et al., 1992; Coplen et al., 1994) and follows the general features of glacial–interglacial cycles, but suggests early Terminations of the glacial

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http://dx.doi.org/10.1016/j.epsl.2014.05.047
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stages thus challenging the Milankovitch theory (Winograd et al., 1992, 2006). The suggestion of early Terminations is disputed with respect to its global or regional significance (Herbert et al., 2001; Lachniet et al., 2011; Shakun et al., 2011). The interpretation of Winograd et al. (1992, 2006) considers the Devils Hole oxygen isotope signal to reflect only atmospheric paleotemperature variability, through the effect of temperature on rainfall $\delta^{18}O$ (Dansgaard, 1964), since the groundwater temperature is thought to have been constant due to the large size of this regional aquifer (Coplen, 2007). Additional effects on rainfall, and therefore groundwater, $\delta^{18}O$ value may be due to the amount effect (Dansgaard, 1964; Rozanski et al., 1993), local re-cycling of rainwater (Koster et al., 1993; Lachniet, 2009), or a change in the moisture source. These have rarely been taken into account in the interpretation of the Devils Hole record. Contrary to the assumptions of Winograd et al. (1992, 2006) and Coplen (2007), Herbert et al. (2001) suggested that the Devils Hole record reflects a regional climate signal possibly through the effect of changing sea surface temperatures at the moisture source at the Pacific coast, but may also include more localized effects such as the possibility of changing groundwater temperature related to climatic changes; if true, this would strongly impact on the interpretation of the Devils Hole oxygen isotope record.

In addition to assuming that the groundwater temperature remained constant at the present-day level of ~34 °C (Coplen et al., 1994), calcite precipitation was thought to occur at isotopic equilibrium. Equilibrium refers to complete oxygen isotope exchange between dissolved inorganic carbon (DIC) and water which is expected when mineral growth is slow relative to the isotope exchange reaction; a system is close to the thermodynamic equilibrium when the rates of the forward and back reactions are similar:

$$Ca^{2+} + 2HCO_3^- \leftrightarrows CaCO_3 + CO_2 + H_2O \tag{1}$$

Eq. (1) reflects the net reaction of several reaction pathways in the $CO_2$–$H_2O$–$CaCO_3$ system (see e.g., Plummer et al., 1978 for more details). In the case of similar forward and back reaction rates in Eq. (1) the potential isotopic preference in ion attachment onto the growing mineral (precipitation) is balanced by an opposite isotopic discrimination during detachment of ions (dissolution; e.g., DePaolo, 2011). The extremely slow growth rate (~0.7 μm/a) of Devils Hole mammillary calcite makes it likely to satisfy these conditions (Watkins et al., 2013). However, given the assumption of constant water $\delta^{18}O$ throughout the Holocene (Coplen, 2007), mid-Holocene calcite is ~1.5‰ more enriched in $^{18}O$ than expected at the modern groundwater temperature, based on the common thermometer calibrations (such as of Kim and O'Neil, 1997). This discrepancy raises doubt with respect to the oxygen isotope thermometer calibration and demands a thorough assessment of the assumptions used in the interpretation of the Devils Hole calcite data.

In this study we use carbonate clumped isotopes to examine whether Devils Hole calcite indeed reflects isotopic equilibrium by quantifying the temperature of calcite formation and testing the assumption of constant water temperature over glacial–interglacial cycles. Carbonate clumped isotope thermometry measures the chemical bonding between $^{13}C$ and $^{18}O$ within the carbonate crystal lattice which is quantified via the $\Delta_{47}$ value (see Affek and Eiler, 2006; Huntington et al., 2009):

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

$\Delta_{47}$ is calculated from the measured ratios ($R^i$) of masses 45, 46 and 47 to mass 44 and by calculating $R^{13}$ ($^{13}C/^{12}C$) and $R^{18}$ ($^{18}O/^{16}O$) from $R^{45}$ and $R^{46}$ assuming random distribution. $R^{17}$ is calculated from $R^{18}$ assuming a mass-dependent relationship between $^{18}O$ and $^{17}O$. The $\Delta_{47}$ value reflects the temperature of mineral formation at equilibrium, providing a paleotemperature proxy (Eiler and Schauble, 2004; Ghosh et al., 2006; Eiler, 2007, 2011; Affek, 2012). The main advantage of the clumped isotope approach compared to $\delta^{18}O$ is that it is independent of the oxygen isotope composition of the water from which the mineral grows, so that the assumption of constant temperature can be directly evaluated.

A wide variety of biogenic and abiogenic $CaCO_3$, both calcite and aragonite, has been observed to follow the same clumped isotope thermometer calibration (Eiler, 2007, 2011; Zaarur et al., 2013) suggesting an equilibrium relationship. Clumped isotope deviations from equilibrium, such as observed in speleothems (Affek et al., 2008; Meckler et al., 2009; Daëron et al., 2011; Wainer et al., 2011; Kluge and Affek, 2012; Kluge et al., 2013), are typically large and therefore easily identified. In stalagmites, rapid degassing of $CO_2$ from a thin water film and fast carbonate precipitation often do not allow sufficient time for isotopic equilibration between DIC and water (for time scales see e.g., Dreybrodt and Scholz, 2011; Uchikawa and Zeebe, 2012; Watkins et al., 2013). In these cases higher $\delta^{18}O$ and lower $\Delta_{47}$ values are observed (e.g., Daëron et al., 2011; Kluge and Affek, 2012). Thus, the combination of clumped and oxygen isotopes in Devils Hole samples gives insight into the type of isotope fractionation (i.e., equilibrium versus non-equilibrium) during calcite formation and improves the understanding of the 570 kyr-long Devils Hole proxy record.

## 2. Study site and samples

The Devils Hole system (116°15′W, 36°25′N) is located in the Amargosa Desert of southern Nevada, about 325 km east of the California coastline. It comprises two caves within 200 m distance, Devils Hole and Devils Hole #2, that formed due to the opening of two north-east striking fractures in Cambrian limestone and dolostone. The caves consist of few cave chambers above the present-day water-table, but are predominantly water-filled as they are part of the discharge area of a large groundwater aquifer (12 000 km$^2$). The aquifer is recharged mainly by winter and spring snow and rainfall at the 3600 m-high Spring Mountains located ~50 km east of Devils Hole (Winograd et al., 1998; Coplen, 2007). The precipitation derives from a Pacific moisture source (Winograd et al., 1988, 1998; Herbert et al., 2001), and the character of moisture supply is assumed to have been similar in the past (Herbert et al., 2001; Kulongoski et al., 2009). More specifically, the tropical Pacific was identified as principal source region for moisture transported to the Great Basin (Lyle et al., 2012) with enhanced rainfall in the Devils Hole region during El Niño years (Winograd et al., 1998, 2006).

The groundwater is slightly super-saturated with respect to calcite resulting in precipitation of up to 40 cm thick mammillary calcite crust covering the fissure walls. The calcite grew continuously for the last 570 kyr at a very low rate (~0.7 μm/a; Winograd et al., 1992). The slow growth is likely related to the only marginally super-saturated groundwater (modern saturation index: 0.16–0.21; Coplen, 2007). In the part of Devils Hole which is exposed to sunlight due to a collapse of the cave roof, calcite growth ceased at about 60 ka; in the aphotic part of the system, in Devils Hole #2, it ceased at ~4.5 ka. It has been speculated that this is probably due to inhibition of calcite growth by organic molecules that formed after photosynthetic activity developed in the water-filled fracture when it was exposed to sunlight (Riggs et al., 1994; Plummer et al., 2000; Winograd et al., 2006).