Controls on the stable isotope compositions of travertine from hyperalkaline springs in Oman: Insights from clumped isotope measurements

E.S. Falk a*, W. Guo a, A.N. Paukert b,c, J.M. Matter b,d, E.M. Mervine a,c, P.B. Kelemen b

a Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA

b Lamont-Doherty Earth Observatory, Columbia University, 61 Route 9W, Palisades, NY 10964, USA

c California State University Sacramento, 6000 J Street, Sacramento, CA 95819, USA.

d University of Southampton, University Road, Southampton SO17 1BJ, UK

e De Beers Marine, Golf Park 2, Raapenberg Road, Pinelands, 7405, Cape Town, South Africa

*Corresponding author. Current address: North Carolina State University, 2800 Faucette Drive, Raleigh, NC 27695, USA. esfalk@ncsu.edu. +1 919 515 3711
Abstract

Carbonate formation at hyperalkaline springs is typical of serpentinization in peridotite massifs worldwide. These travertines have long been known to exhibit large variations in their carbon and oxygen isotope compositions, extending from apparent equilibrium values to highly depleted values. However, the exact causes of these variations are not well constrained. We analyzed a suite of well-characterized fresh carbonate precipitates and travertines associated with hyperalkaline springs in the peridotite section of the Samail ophiolite, Sultanate of Oman, and found their clumped isotope compositions vary systematically with formation environments. Based on these findings, we identified four main processes controlling the stable isotope compositions of these carbonates. These include hydroxylation of CO$_2$, partial isotope equilibration of dissolved inorganic carbon, mixing between isotopically distinct carbonate end-members, and post-depositional recrystallization. Most notably, in fresh crystalline films on the surface of hyperalkaline springs and in some fresh carbonate precipitates from the bottom of hyperalkaline pools, we observed large enrichments in $\Delta^{47}$ (up to ~0.2‰ above expected equilibrium values) which accompany depletions in $\delta^{18}$O and $\delta^{13}$C, yielding about 0.01‰ increase in $\Delta^{47}$ and 1.1‰ decrease in $\delta^{13}$C for every 1‰ decrease in $\delta^{18}$O, relative to expected equilibrium values. This disequilibrium trend, also reflected in preserved travertines ranging in age from modern to ~40,000 years old, is interpreted to arise mainly from the isotope effects associated with the hydroxylation of CO$_2$ in high-pH fluids and agrees quantitatively with our theoretical prediction. In addition, in some fresh carbonate precipitates from the bottom of hyperalkaline pools and in subsamples of one preserved travertine terrace, we observed additional enrichments in $\Delta^{47}$ at
intermediate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, consistent with mixing between isotopically distinct
carbonate end-members. Our results suggest that carbonate clumped isotope analysis can
be a valuable tool for identifying and distinguishing processes not readily apparent from
the carbonate bulk stable isotope compositions alone, e.g., kinetic effects or mixing of
different carbonate end-members, which can significantly alter both the apparent
formation temperatures and apparent radiocarbon ages. The isotope trends observed in
these travertine samples could be applied more broadly to identify extinct hyperalkaline
springs in terrestrial and extraterrestrial environments, to better constrain the formation
conditions and post-depositional alteration of hyperalkaline spring carbonates, and to
extract potential paleoclimate information.

1. Introduction
1.1 Carbonate formation in peridotite-hosted hyperalkaline springs

Springs emanating from serpentinized peridotite in the Samail ophiolite, Sultanate
of Oman, are characterized by high pH (~11-12), high Ca$^{2+}$ concentrations, and almost no
dissolved inorganic carbon (DIC). These hyperalkaline springs react with atmospheric
CO$_2$, resulting in rapid precipitation of calcium carbonate and formation of extensive
travertine terraces (Neal and Stanger 1985; Clark and Fontes, 1990; Kelemen and Matter,
2008; Matter and Kelemen, 2009; Kelemen et al., 2011; Paukert et al., 2012; Chavagnac
et al. 2013a,b; Mervine et al., 2014, 2015).

The development of these Ca$^{2+}$-OH rich waters is typical of serpentinization in
peridotite massifs worldwide (e.g., Barnes et al., 1967; Barnes and O'Neil, 1969; Barnes
et al., 1978; Neal and Stanger, 1985; Bruni et al., 2002; Neal and Shand, 2002; Marques
et al., 2008; Szponar et al., 2013; Cardace et al., 2015). Such ultramafic systems have
been the subject of diverse studies, with much interest in fate of carbon in these
environments. The rapid uptake of CO$_2$ during natural carbonation of peridotite,
estimated to currently be $\sim$10$^3$ tons of CO$_2$ km$^{-3}$ yr$^{-1}$ in Oman, has been viewed as a
promising analog for mineral carbon sequestration (e.g., Cipolli et al., 2004; Kelemen
and Matter, 2008; Wilson et al., 2009). The development of hyperalkaline fluids during
serpentinization has also been suggested as possible driver of carbonate precipitation and
methane generation on Mars (e.g., Niles et al., 2005; Oze and Sharma, 2005; Ehlmann et
al., 2010; Etiope et al., 2013), attracting attention to terrestrial hyperalkaline springs as
potential Martian analogs (e.g., Szponar et al., 2013). In addition, there have been
attempts to reconstruct paleoclimate in Oman (e.g. periods of aridity or humidity) based
on variations in travertine morphology and the bulk stable isotope compositions of
carbonates (Clark and Fontes, 1990).

Unlike typical travertines precipitated by degassing of CO$_2$ from calcium- and
bicarbonate-rich waters of hydrothermal origin, which may record apparent equilibrium
oxygen and clumped isotope compositions near spring vents (e.g., Kele et al., 2015), the
isotope compositions of travertines formed at hyperalkaline springs usually deviate
significantly from expected equilibrium values. Previous studies of peridotite-hosted
travertines in Oman revealed positive correlations between their $\delta^{13}$C and $\delta^{18}$O values,
with $\delta^{13}$C vs. $\delta^{18}$O slope of $\sim$1.3 (Clark and Fontes, 1990; Clark et al., 1992; Kelemen et
al., 2011; Mervine et al., 2014). The youngest travertines are often characterized by large
depletions in $^{13}$C and $^{18}$O (Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014),
while preserved travertines generally exhibit relatively higher $\delta^{13}$C and $\delta^{18}$O values that
may extend to values consistent with expected equilibrium with observed spring-water \(^{18}\)O and temperatures and atmospheric \(^{13}\)C (Neal and Stanger, 1985; Clark et al., 1992; Matter, 2005). Similar correlated depletions in \(^{13}\)C and \(^{18}\)O have been observed worldwide in other carbonates precipitated during interaction between alkaline waters and atmospheric CO\(_2\). For example, the \(^{13}\)C and \(^{18}\)O values of fresh carbonate precipitates and travertines from hyperalkaline springs in northern California overlap significantly with values observed in Oman (O’Neil and Barnes, 1971; Kelemen et al., 2011). These depletions in \(^{13}\)C and \(^{18}\)O have typically been interpreted as a kinetic isotope effect resulting from CO\(_2\) uptake from the atmosphere (O’Neil and Barnes, 1971; Clark et al., 1992; Wilson et al., 2010). In some cases depleted isotopic signatures in carbonates precipitated in alkaline environments may also be derived from nearby carbonate sediments, as was initially suggested for surface calcium carbonates associated with weathering of chrysotile tailings in northern British Columbia (Wilson et al., 2009).

1.2 Carbonate clumped isotope geochemistry

The carbonate clumped isotope thermometer is a relatively new paleothermometer based on the tendency of \(^{13}\)C and \(^{18}\)O isotopes to preferentially bond to one another (or “clump”) within the CO\(_3^{2-}\) groups under thermodynamic equilibrium. This property is commonly measured as ‘\(\Delta_{47}\),’ the excess of mass-47 isotopologue (primarily \(^{13}\)C\(^{18}\)O\(^6\)O) in the CO\(_2\) evolved from phosphoric acid digestion of solid carbonate relative to the abundances expected for a stochastic distribution of all isotopes (Ghosh et al., 2006; Eiler, 2007; Eiler, 2011; Huntington et al., 2009):
$$\Delta_47 = \left[ \left( \frac{R_{47}}{R_{47}^*} - 1 \right) - \left( \frac{R_{46}}{R_{46}^*} - 1 \right) - \left( \frac{R_{45}}{R_{45}^*} - 1 \right) \right] \times 1000 \quad (\text{Equation 1a})$$

where \( R_i \) is the measured ratio of the isotopologue of mass \( i \) and \( R_i^* \) is the ratio for a stochastic distribution. i.e., \( \Delta_47 = \left[ \frac{R_{47}}{2R_{13} \times R_{18} + 2R_{17} \times R_{18} + R_{13} \times (R_{17})^2} - \frac{R_{46}}{2R_{13} + 2R_{17}} \right] \times 1000 \quad (\text{Equation 1b}).$$

Unlike conventional carbonate-water oxygen isotope thermometry, the extent of this clumping effect, under thermodynamic equilibrium, depends only on the equilibration temperature and not on the isotopic composition of the waters from which the carbonate precipitated. This makes it a valuable tool for a variety of applications, especially in cases where the isotopic composition of the parent waters are difficult to constrain, e.g. paleoclimate, paleoaltimetry, diagenesis, and low grade metamorphism (see reviews in Eiler, 2011; Affek, 2012; Huntington and Lechler, 2015).

Although inter-laboratory differences remain in the calibration of the carbonate clumped isotope paleothermometer, calibrations among a variety of natural and synthetic carbonates have so far yielded remarkably consistent results within individual laboratories considering the range of materials studied (e.g., Ghosh et al., 2006; Dennis and Schrag, 2010; Tripati et al., 2010; Eiler, 2011; Eagle et al., 2013; Grauel et al., 2013; Henkes et al., 2013; Zaarur et al., 2013; Defliese et al., 2015; Kele et al., 2015; Kluge et al., 2015). Mostly notably, the clumped isotope compositions of some carbonate materials that were known to be affected by kinetic effects in bulk stable isotopes, such as certain deep-sea corals, foraminifera and coccoliths, appear to conform to the equilibrium temperature calibration relationship derived from inorganic carbonates precipitated in the
laboratory (e.g., Tripati et al., 2010; Thiagarajan et al., 2011). However, there is increasing evidence that disequilibrium clumped isotope effects also exist in nature, especially for several types of carbonates, e.g. speleothems, cryogenic carbonates (e.g., Affek et al., 2008; Guo 2008; Daeron et al., 2011; Wainer et al., 2011; Kluge and Affek, 2012; Kluge et al., 2014; Affek et al., 2014), some shallow-water and cold-water corals (Saenger et al., 2012; Spooner et al., 2016). These disequilibrium clumped isotope effects, if not corrected for, would lead to systematic over-estimation (e.g. for speleothems and cryogenic carbonates) or under-estimation (e.g. for some corals) of the carbonate formation temperatures derived from the clumped isotope thermometer. Our current understanding of the causes of these disequilibrium effects is still limited, but most of these effects are thought to be related to the kinetic isotope fractionations associated with the CO$_2$ hydration/hydroxylation reactions and their reverse reactions (e.g., Guo, 2008; Saenger et al., 2012; Affek et al., 2014; Spooner et al., 2016). The same reactions, particularly CO$_2$ hydroxylation, play key roles in carbonate formation during rapid uptake of CO$_2$ at alkaline springs, as in Oman (Clark et al., 1992). Here we present an investigation of the clumped isotope systematics of carbonates formed in hyperalkaline springs in Oman, and discuss the implication of our findings for the interpretation of the isotopic compositions of travertines formed in similar environments.

2. Geologic setting and travertine formation in Oman

The Samail ophiolite, in the Sultanate of Oman and the United Arab Emirates (Figure 1), represents one of the largest exposures of mantle peridotite on land. The mantle peridotite section is composed of residual harzburgites and dunites and is variably
serpenitized, typically ~30-80% (e.g., Boudier and Coleman, 1981; Godard et al., 2000; Monnier et al., 2006; Hanghøj et al., 2010), with completely serpenitized peridotite commonly observed in more altered sections. Much of this serpentine is thought to have formed during suboceanic hydrothermal alteration prior to exposure of the ophiolite on land (e.g., Boudier et al., 2010), but low temperature serpentinization continues today during reaction of meteoric water with peridotite (e.g., Barnes and O’Neil, 1978; Neal and Stanger, 1983; Streit et al., 2012).

This ongoing low temperature alteration of peridotite leads to the formation of hyperalkaline springs and abundant carbonate precipitation via three steps. (1) Meteoric surface waters react with shallow peridotite in an open system that remains in equilibrium with atmospheric CO$_2$ and O$_2$. This results in the formation of waters rich in Mg$^{2+}$-HCO$_3^-$, also known as “Type I” waters (Barnes and O’Neil, 1969). (2) As surface waters percolate deeper into the peridotite, they become isolated from the atmosphere. The formation of Mg-rich alteration products, such as serpentine and Mg-carbonate, in this subsurface environment leads to decreases in concentrations of Mg$^{2+}$ and DIC, while Ca$^{2+}$ continues to accumulate in the groundwater through continued dissolution of peridotite. This results in the formation of alkaline Ca$^{2+}$-OH$^-$ waters, also known as “Type II” waters, characterized by high pH (up to 12), low Eh (approximately -200 mV), and virtually no Mg$^{2+}$ (typically <10$^{-2}$ mmol/L) or DIC (typically ~10$^{-1}$ mmol/L) (Barnes and O’Neil, 1969; Neal and Stanger, 1985; Bruni et al., 2002; Paukert et al., 2012; Chavagnac et al., 2013b). (3) When these Ca$^{2+}$-OH$^-$ waters reach the surface as hyperalkaline springs, rapid precipitation of calcium carbonate results from reaction with CO$_2$, either by
direct uptake of atmospheric CO$_2$ or mixing with shallow groundwater or surface waters containing ~3-5 mmol/L DIC (Paukert et al., 2012).

Alkaline springs of this type are common throughout the peridotite section of the Samail ophiolite, with close to 100 such springs identified in previous studies (e.g., Stanger, 1985; Neal and Stanger, 1985; Kelemen and Matter, 2008; Paukert et al., 2012; Chavagnac et al., 2013b). Where alkaline spring water comes in contact with atmospheric CO$_2$, crystalline films of calcium carbonate may form on the surface of pools. This reaction is rapid enough that calcium carbonate crusts ~0.5mm thick re-form on the surface of the pools within a couple days when they are removed by rainstorms or manually. In many locations, these alkaline springs form a series of striking, milky-blue pools lined with white unconsolidated calcium carbonate precipitates, particularly where springs emerge along wadi (stream) beds. Alkaline spring water may also flow along the surface of travertine terraces in shallow trickles without the development of larger pools or may form speleothem-like carbonate structures where eroded peridotite outcrops form overhangs that allow alkaline water to drip freely. In previous studies of carbonate mineralogy at alkaline springs, fresh calcium carbonate precipitates have been found to be mixtures of calcite and aragonite, with calcite more common in surface films and aragonite more common in bottom deposits (Paukert et al., 2012; Chavagnac et al., 2013a; Mervine et al., 2014).

Over time, calcium carbonate precipitation associated with these hyperalkaline springs has resulted in the build-up of extensive travertine terraces, typically ~200,000 m$^2$ in area and ~1 m thick, in areas surrounding active springs (Kelemen and Matter, 2008). Radiometric dating and measurements of layer thickness within travertine terraces
suggests that travertine deposition has been ongoing for at least 50,000 years, with average deposition rates of ~0.1-0.3 mm/year (Kelemen and Matter, 2008; Mervine et al., 2014). Clark and Fontes (1990) had previously argued that surficial travertine deposits in Oman were only deposited and preserved during periods of hyper-aridity, but subsequent studies have identified travertine terraces with $^{14}$C ages that fill in the gaps in the Clark and Fontes (1990) record (Kelemen and Matter, 2008; Mervine et al., 2014).

3. Material and Methods

3.1 Description of carbonate samples

A total of 29 samples of fresh carbonate precipitates from alkaline springs and 14 preserved travertines were collected from 9 locations throughout the southern portion of the Samail ophiolite (Figure 1) over several field seasons, each January between 2007 and 2012. Sample locations and descriptions are presented in Table 1, and photos of some sampling locations are shown in Figure 2. Many of these samples (10 fresh carbonate precipitates and 14 travertines, as indicated in Table 1) have been included in previous studies of hyperalkaline springs and travertine formation in Oman, in which their mineralogical composition, carbon and oxygen isotope composition, and/or $^{14}$C ages were reported (Kelemen et al., 2011; Paukert et al., 2012; Falk, 2013; Mervine et al., 2014). None of the samples have been analyzed before for their clumped isotope compositions. In this study, we performed clumped isotope analysis on 28 of these carbonate samples and only bulk carbon and oxygen isotope analysis on the other 15 samples.

The fresh carbonate precipitates we collected from hyperalkaline springs can be grouped into two main types: (1) “surface films”—thin crystalline films or crusts formed
at the surface of hyperalkaline springs (e.g., Figure 2c)—and (2) “bottom floc”—the
unconsolidated carbonate lining hyperalkaline spring pools and outlet channels. Bottom
floc samples can be further divided based on their depositional environments. Some are
found in larger hyperalkaline spring pools within wadi (stream) beds (e.g., Figure 2a),
while others form in smaller pools and thin flows along the surface of travertine terraces
(e.g., Figure 2b,d). All surface films were collected directly at the hyperalkaline spring
source. Bottom floc samples were collected either directly at the hyperalkaline spring
source or at downstream locations close enough to the spring that water pH remained
above 11. Carbonates collected at the exact same location as water samples are listed
with their corresponding water samples in Table 2. These include “flow path” samples—
samples collected downstream from the alkaline spring outlet, with distance from the
spring indicated in Table 2.

The travertine samples in this study include recently-formed travertine layers
from areas of active travertine deposition and older laminated travertine terraces (Figure
2f). Specifically, the older travertine samples consist of carefully subsampled layers of a
~2m thick travertine section from Al Bana (i.e., the Misht Travertine location; Mervine et
al. 2014) and a ~1m thick travertine section from the Wadi Uqaybah travertine, both of
which were previously described and radiocarbon dated by Mervine et al. (2014). There
are no active hyperalkaline springs flowing along the surfaces of these older travertines
where these samples were collected, but they are located in the general vicinity of active
hyperalkaline springs.

Sample collection and processing methods for fresh precipitates, preserved
travertines, and associated water samples are described in detail by Paukert et al. (2012)
and Mervine et al. (2014). Briefly, fresh precipitates collected from hyperalkaline pools were allowed to dry at ambient conditions and later dried in a 40°C oven. Because of the very fine-grained nature of these precipitates, crushing and mechanical powdering of these samples was not necessary prior to mineralogical and isotopic analyses. Preserved travertine rock samples collected in 2007-2009 were crushed in a jaw crusher and powdered in a puck mill or with an agate mortar and pestle. Layers from travertines collected in 2010 were carefully subsampled at millimeter scales using a micromill, as previously described in Mervine et al. (2014).

### 3.2 Properties of spring water

In situ and laboratory-based measurements were made on spring water from hyperalkaline pools and flow paths along the surface of travertine terraces, to determine water temperature, pH, major element chemistry and stable isotopic compositions (Table 2). These field data and water samples were obtained in 2008-2012 (year of collection indicated by sample prefix), during the same field seasons as the carbonate samples described above, and several pools (“sites”) were re-visited over the course of multiple field seasons. Many of the fresh carbonate samples discussed in this study were collected from the same pools as the spring water samples, as indicated in Table 2. In most of those cases, collection of water samples and in situ measurements of pH were made at the time of collection of fresh carbonate precipitates. Additional data for some of the water samples (e.g., conductivity, oxidation-reduction potential, and major and trace element concentrations) have been reported previously in Paukert et al. (2012), as indicated in Table 2.
In situ measurements of the pH and temperature of alkaline springs were conducted using a WTW Multi 3400i multi-parameter field meter (Paukert et al., 2012). Major cation compositions were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Horiba Jobin-Yvon Activa M spectrometer at Columbia University, by inductively coupled plasma atomic absorption spectrometry on a Perkin-Elmer AAnalyst 800 spectrometer at CUNY Queens College, and an inductively coupled plasma mass spectrometer at Arizona State University. DIC concentrations were measured at Arizona State University on an OI Analytical Model 1010 Wet Oxidation TOC Analyzer for samples from the 2009 and 2010 field season and at Columbia University via acidification on a UIC CM5230 carbon analyzer for samples from the 2012 field season. The analytical precisions were ±2% and ±1% (relative standard deviation) for major cation concentrations and DIC concentration measurements, respectively.

δ¹⁸O and δD of water, and δ¹³C of DIC were measured by isotope ratio mass spectrometry (IRMS) in the Environmental Isotopes Laboratory at the University of Waterloo. δ¹⁸O of water was determined by the CO₂ equilibration method (Epstein and Mayeda, 1953), using a VG 903 mass spectrometer for samples from the 2008 field season (prefix “OM08-“) and using a Micromass IsoPrime mass spectrometer for all other samples. δD of water was analyzed by the chromium reduction method on a Eurovector Euro 3000 Elemental Analyzer coupled to a Micromass IsoPrime mass spectrometer (Gehre et al., 1996). For carbon isotope measurements of DIC, water was reacted under vacuum with anhydrous (100%) H₃PO₄ (McCrea, 1950), and the liberated CO₂ was then directly released into a Micromass IsoPrime mass spectrometer via a
Gilson 222XL auto-sampler. The overall analytical precisions were ±0.2‰, ±0.8‰, and ±0.2‰ (1 S. D.) for δ^{18}O_{water}, δD, and δ^{13}C_{DIC}, respectively. The isotopic data are reported relative to Vienna Standard Mean Ocean Water (VSMOW) and Vienna Pee-Dee Belemnite (VPDB).

3.3 Carbonate mineral identification

For fresh carbonate precipitates collected in 2012 that were subject to clumped isotope analysis, calcium carbonate minerals were identified by Raman spectroscopy using a Horiba LabRAM HR confocal Raman spectrometer at Woods Hole Oceanographic Institution (WHOI). Spectra were collected for 5 s with 3 accumulations averaged for each analysis spot. Each sample was analyzed at four spots and each spectrum was classified as calcite, aragonite, or a very fine-grained mixture of both in order to reflect the relative proportions of each mineral.

The mineralogy of samples collected in 2007-2011 was determined by powder X-ray diffraction (XRD) and reported in detail in previous studies (Kelemen et al., 2011; Paukert et al., 2012; Falk, 2013; and Mervine et al., 2014). Semi-quantitative estimates of mineral proportions based on relative peak intensities of X-ray diffraction spectra were used to classify each mineral as major (> ~ 20%) or minor (< ~ 10%) in these samples, as reported in Table 1.

3.4 Radiocarbon dating of travertines

All ^{14}C ages of preserved travertines were determined at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at Woods Hole.
Oceanographic Institution, including data reported in previous studies and new ages obtained for this study. Most of the $^{14}$C ages reported in Table 1 were obtained by Mervine et al. (2014), and detailed methods are reported in that publication. Additional $^{14}$C ages were obtained on recent travertine samples OM07-34C and OM08-200 in 2008 and reported in Kelemen et al. (2011). Two travertine terrace subsamples previously analyzed by Mervine et al. (2014), OM10-32C-8 and OM10-32C-10, were submitted to NOSAMS for re-analysis in 2014, and these new data are reported in Table 1. All $^{14}$C data were corrected for isotopic fractionation using $\delta^{13}$C values measured on the accelerator. $^{14}$C ages were calculated using 5568 years as the half-life and converted to calibrated ages using the Calib 7.1 Program with the IntCal13 calibration curve (Reimer et al., 2013). Because alkaline spring water emerges with essentially no dissolved carbon and most carbonates form from direct uptake of atmospheric CO$_2$, no correction for the possible effects of dead carbon is made in the calculation of $^{14}$C ages (Mervine et al., 2014).

3.5 Stable isotope measurements of carbonates

3.5.1 Carbon and oxygen isotope measurement

Stable carbon and oxygen isotope compositions were determined for all carbonate samples. $\delta^{13}$C and $\delta^{18}$O data for fresh carbonate precipitates collected along alkaline spring flow paths at Falaij and Al Bana travertine sites in 2012 were obtained in the Environmental Isotopes Laboratory at the University of Waterloo using a GVI IsoPrime continuous flow isotope ratio mass spectrometer system (CF-IRMS) following automated phosphoric acid digestion at 90°C. The external precisions for these measurements are
±0.2‰ (1 S.D.) for δ¹⁸O and ±0.1‰ (1 S.D.) for δ¹³C. Bulk stable isotopic data (δ¹³C and δ¹⁸O) for two of these samples and all other carbonate samples were obtained at Woods Hole Oceanographic Institution simultaneously with Δ₄₇, as part of the clumped isotope measurement, and were normalized by reference to the carbonate standard NBS-19 analyzed in each analytical session, with precisions of ±0.08‰ and ±0.10‰ (1 S.D.) respectively. All the carbonate isotope values are reported relative to Vienna Pee-Dee Belemnite (VPDB) in Table 3.

3.5.2 Clumped isotope measurement: Method

Clumped isotope analyses were performed at Woods Hole Oceanographic Institution on a Thermo MAT-253 stable isotope mass spectrometer coupled to an automated sample digestion and purification line (Thornalley et al., 2015; Spooner et al., 2016). For each carbonate measurement, 3-5 mg of powdered sample material are loaded into silver capsules for in vacuo digestion in a common acid bath of 103% phosphoric acid (ρ=1.92 g/cm³) at 90°C for 20 minutes. During this reaction, evolved CO₂ is continuously frozen into a trap immersed in a dewar of liquid nitrogen (LN2), after passing through a cryogenic trap maintained at -78°C. Upon completion of the acid digestion step, the collection trap is warmed to -78°C, and the CO₂ is transported by a He carrier gas at a controlled flow rate of 30 ml/minute through a custom-made 60 cm long gas chromatography (GC) column (Porapak Q, 50-80 mesh) held at -20°C before being collected in a second LN2 trap. After the He carrier gas is pumped away, the purified CO₂ is again warmed to -78°C and transferred to a small glass LN2 trap. The CO₂ is then allowed to expand into the sample bellow of the mass spectrometer. All gas standards
(i.e. heated gases and equilibrated gases; see section 3.5.3) used in the construction of the absolute reference frame are introduced and purified in the same manner as CO$_2$ derived from carbonate samples: passing through a -78°C trap and allowed to collect in a LN2 trap for 20 minutes before further GC and cryogenic purification. Purified CO$_2$ were measured against a bottle of working reference CO$_2$ (Oztech CO$_2$, $\delta^{18}$O$_{VSMOW} = 25.04\%$, $\delta^{13}$C$_{VPDB} = -3.63\%$) at a bellow pressure resulting in a signal of 12V on mass-44. Each clumped isotope measurement consists of 6 acquisitions, with 9 cycles of sample-reference comparison (20s of integration time) in each acquisition.

3.5.3 Clumped isotope measurement: Data reduction

Carbonate samples were analyzed over the course of three analytical sessions (January-February, March-April, and July 2014), with each sample analyzed 3-8 times. Four measurements from the first analytical session were excluded from the final sample averages because $\delta^{13}$C and $\delta^{18}$O values were several permil higher than other replicate measurements and/or $\Delta_{47}$ values differed significantly (up to 0.11‰) from other replicate measurements. These discrepancies were due to variations in the He carrier gas flow rate prior to installation of a mass flow controller. As a result, only two replicates are included in the averages for two of the travertine samples because insufficient sample material remained for additional replicate measurements.

Pure CO$_2$ gases of different bulk isotope compositions equilibrated at 1000°C and 25°C or 40°C (commonly referred to as ‘heated gases’ and ‘equilibrated gases’) were analyzed on a daily basis during all three analytical sessions, to correct for instrument nonlinearities and to construct the absolute reference frame (Huntington et al., 2009;
Dennis et al., 2011). For heated gases, aliquots of CO₂, including isotopically depleted CO₂ derived from Oman travertine sample OM07-34C, were sealed in quartz tubes and heated in a muffle furnace set at 1000°C for at least 1 hour. Equilibrated gases consisted of CO₂ equilibrated with water maintained at either 40°C prior to May 2014 (sessions 1 and 2) or 25°C subsequently (session 3). Two in-house carbonate standards, NBS-19 and 102-GC-AZ01, were also analyzed on a nearly daily basis to monitor system stability within each analytical session and to evaluate potential inter-laboratory differences in clumped isotope measurements.

Carbonate clumped isotope data from these sessions were projected into the absolute reference frame of Dennis et al. (2011), based on the heated and equilibrated gases analyzed during a given session (See Supplementary Table S1 for heated and equilibrated gas analyses, slopes, and intercepts for each session). During the first analytical session, the flow rate of the He carrier gas during the GC purification step occasionally drifted to lower values (e.g., 24 ml/min instead of 30 ml/min). This resulted in significantly higher measured values of δ¹³C, δ¹⁸O, and Δ₄₇ for some heated gas and carbonate analyses. These data were excluded from the construction of the gas reference frame for this session, but are still reported in Supplementary Table S1 for reference.

Addition of a mass flow controller to maintain the He flow at 30 ± 1 ml/min eliminated this problem in subsequent analytical sessions. By convention, carbonate Δ₄₇ values are normalized to acid digestions performed at 25°C by addition of an acid digestion correction factor. We use an acid digestion correction factor of 0.092‰, determined by Henkes et al. (2013) where the analytical setup was very similar to that used for our analyses at WHOI.
Measurements of two in-house carbonate standards in the three analytical sessions yielded Δ47 values of 0.391 ± 0.019‰ (1 S.D., n=8), 0.422 ± 0.021‰ (n=17) and 0.424 ± 0.016‰ (n=12) for NBS19, and 0.725 ± 0.018‰ (n=28), 0.737 ± 0.020‰ (n=30) and 0.733 ± 0.024‰ (n=13) for 102-GC-AZ01, respectively. These values are either within or close to the range of the average values reported in a recent inter-laboratory study, 0.392 ± 0.017‰ (1 S.D.) for NBS19 and 0.713± 0.12‰ (1 S.D.) for 102-GC-AZ01 (Dennis et al., 2011). The inter-laboratory difference in clumped isotope measurements is currently a subject of extensive investigation in the clumped isotope community, and is suspected to be related to the difference in the exact analytical protocols in different laboratories (e.g., during the acid digestion process, Came et al. 2014; Defliese et al. 2015).

To account for these inter-laboratory difference in clumped isotope measurements, we applied an additional correction to our clumped isotope data in this study, based on a linear function required to bring these carbonate standards’ clumped isotope values in each session into agreement with their previously reported values (Spooner et al. 2016). This approach is similar to the method Dennis et al. (2011) outlined for constructing a secondary reference frame based on carbonate standards. The robustness of this correction procedure has been evaluated in a recent inter-laboratory comparison exercise between the WHOI and Caltech laboratories, where the same powdered carbonate samples were distributed and analyzed at both labs (Spooner et al., 2016). Excellent agreement was observed between the two labs, when the WHOI data were corrected based on the reported Δ47 values for NBS19 and 102-GC-AZ01 obtained at Caltech (0.392‰ and 0.724‰ respectively; Dennis et al., 2011; Spooner et al., 2016). We adopt the same reported Δ47 values for these two standards during the data correction.
in this study. Note, the magnitude of this additional correction, an average of 0.005‰ and up to a maximum of 0.015‰, is over one order of magnitude smaller than the range of $\Delta_{47}$ variations observed in our carbonate samples (0.21‰; see section 4.3.2), and thus it should not affect the conclusion of this study.

4. Results

4.1 Alkaline spring conditions

Physiochemical conditions of the alkaline spring water, including temperature, pH, $\delta^{18}$O$_{\text{water}}$, $\delta$D, $\delta^{13}$C$_{\text{DIC}}$, and concentrations of DIC, Mg$^{2+}$, and Ca$^{2+}$, are reported in Table 2 and plotted in Figures 3 and 4 and Supplementary Figures S1 and S2.

Spring water temperatures and pH values measured in this study range from 21.7 to 32°C and from 11.2 to 12.1, falling within the temperature and pH ranges previously reported for hyperalkaline springs in Oman (i.e., 17-39°C and 11.0-12.0 for hyperalkaline springs that have not mixed with wadi water; Neal and Stanger, 1985; Paukert et al., 2012; Chavagnac et al., 2013b). The subset of these measurements that were made at the time of collection of fresh carbonate precipitates range from 22.5 to 28.7°C and from 11.2 to 11.6. Some springs were sampled in the same location in multiple years, demonstrating inter-annual variability up to 4.2°C and 0.4 pH units (see samples from the same “Site” in Table 2). All the water samples analyzed in this study were collected in January, but seasonal variations in the spring water temperature and pH observed in previous studies were small. For example, year-round observations of one hyperalkaline spring yielded temperatures of 31-36°C and pH of 11.4 to 11.8 with the exception of rare influxes of fresh surface waters (Neal and Stanger, 1985). Note that carbonate
precipitation may also occur where alkaline spring waters mix with wadi (stream) waters, yielding pH values between 9 and 11 (Paukert et al., 2012; Chavagnac et al., 2013a), but only one of the fresh carbonate precipitates we analyzed (OM11_07Y) was formed at such a location (“Misbit mixing”) with a pH of 10.6 (Table 2).

\[ \delta^{18}O_{\text{water}} \] values of hyperalkaline springs measured in this study range from -1.5‰ to 2.5‰ VSMOW, with an average of 0.1 ± 1.0‰ VSMOW (1 S.D.), consistent with previously published oxygen isotope compositions of hyperalkaline springs in Oman (e.g., average of -1.1 ± 0.8‰ VSMOW (1 S.D.); Neal and Stanger, 1985). \[ \delta D_{\text{water}} \] values of hyperalkaline springs measured in this study range from -8.5‰ to 9.8‰ VSMOW and are strongly correlated with \[ \delta^{18}O_{\text{water}} \]. The isotopic compositions of spring waters lie below the global meteoric water line (GMWL), suggesting evolution along evaporative trends (Figure 3, Craig, 1961). \[ \delta^{13}C_{\text{DIC}} \] values in hyperalkaline springs range from -28.7‰ to -6.0‰ VPDB, with an average of -17.6 ± 4.8‰ (1 S.D.). Inter-annual variability of the isotopic composition of water at individual springs is smaller than the variability between different springs. \[ \delta^{18}O_{\text{water}}, \delta D_{\text{water}} \] and \[ \delta^{13}C_{\text{DIC}} \] values measured in the same pools in different years differ from one another by 0.1 to 1.7‰, 1.1‰ to 7.4‰ and 0.04‰ to 9.2‰, respectively (Table 2).

The chemical and isotopic composition of water samples collected along flow paths emanating from a single alkaline source spring and traveling in shallow flows along the surface of travertine terraces exhibit some characteristics indicating combined effects of progressive evaporation, CO₂ uptake, and carbonate precipitation, but there are no systematic trends common to all flow paths (Figure 4, Figure S2). For example, \[ \delta^{18}O_{\text{water}} \] and \[ \delta D_{\text{water}} \] are strongly correlated and increase along evaporative trends for some flow
paths. pH also decreases with greater distance from the source spring, as would be expected during CO$_2$ uptake or carbonate precipitation, for some but not all flow paths (Figure S2). Similarly, for the two flow paths where DIC concentration data are available, DIC concentration increases slightly overall along the flow paths. Ca concentration generally decreases along the flow path, as would be expected with precipitation of calcium carbonate. Mg concentration remains constant, or increases for flow paths where correlated increases in $\delta^{18}$O$_{\text{water}}$ and $\delta^D_{\text{water}}$ suggest progressive evaporation (Figure S2).

4.2 Carbonate mineralogy and $^{14}$C ages

Carbonate minerals identified by XRD and Raman spectroscopy analysis are presented in Table 1. Fresh precipitates in this study are composed of pure calcite, pure aragonite, and mixtures of calcite and aragonite, with calcite more common in crusts formed at pool surfaces and aragonite more common in fine precipitates found lining alkaline pools and spring outlets. This distribution of calcite and aragonite is consistent with the mineralogy observed in other hyperalkaline springs in Oman (Chavagnac et al., 2013a). In contrast, preserved travertines are predominantly calcite, with minor amounts of aragonite found only in one recently-formed travertine sample (OM09-89C).

The calibrated $^{14}$C ages of fresh carbonate precipitates and of travertine deposits considered in this study, range from modern to 350 years and from modern to 45,000 years, respectively, where “modern” is defined by >95% of the $^{14}$C activity for AD 1950 (Olsson, 1970; Kelemen and Matter, 2008; Kelemen et al., 2011; Mervine et al., 2014; this study). Two of the travertine subsamples (OM10-32C-8 and OM10-32C-10) dated by Mervine et al. (2014) were re-analyzed in this study, yielding calibrated $^{14}$C ages of
18,350 ± 118 (1 S.D.) years and 15,640 ± 126 years, respectively. These ages are different from their previously reported calibrated \(^{14}\)C ages (16,710 ± 133 years and 23,710 ± 215, respectively; Mervine et al., 2014), which could be related to heterogeneity of the travertine samples. Because the \(^{14}\)C analyses in this study were performed on the same aliquots of sample powders used in the clumped isotope analyses, we refer to these \(^{14}\)C ages in Table 1 and in the following discussion.

4.3 Stable isotope compositions of carbonates

We present the results of stable isotope analyses (\(\delta^{13}\)C, \(\delta^{18}\)O and \(\Delta_{47}\)) of fresh carbonate precipitates and preserved travertines in Table 3. Raw data of the clumped isotope analyses, including all analyses of samples, carbonate standards, heated gases, and equilibrated gases, are reported in Supplementary Table S1.

4.3.1 Oxygen and carbon isotope compositions

\(\delta^{18}\)O and \(\delta^{13}\)C values of fresh carbonate precipitates and preserved travertines range from highly depleted values (e.g., \(\delta^{18}\)O\textsubscript{VPDB} and \(\delta^{13}\)C\textsubscript{VPDB} as low as -16.9‰ and -27.2‰ respectively) to values approaching expected equilibrium with spring waters (e.g., \(\delta^{18}\)O\textsubscript{VPDB} = 0‰ and \(\delta^{13}\)C\textsubscript{VPDB} = -4‰), with a strong positive correlation between the two (overall \(\delta^{13}\)C vs. \(\delta^{18}\)O slope of 1.1, \(R^2=0.83\); Figure 5a). The \(\delta^{18}\)O and \(\delta^{13}\)C values recorded in these samples overlap with that observed in previous studies of Oman travertine (-17 to +6‰ in \(\delta^{18}\)O, -33 to +3‰ in \(\delta^{13}\)C, and \(\delta^{13}\)C vs. \(\delta^{18}\)O slope of 1.3, Clark and Fontes, 1990; Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014). The bulk oxygen and carbon isotopic compositions of fresh carbonate precipitate samples
collected in 2009-2010 and all of the preserved travertine samples in this study were also analyzed in previous studies. δ^{13}C and δ^{18}O derived from our clumped isotope analyses typically fall within 0.3‰ of the previously reported values (Supplementary Figure S3; Kelemen et al., 2011; Mervine et al., 2014). Greater differences were observed between the isotopic compositions derived from clumped isotope analyses at WHOI and those measured at the University of Waterloo: for the two samples analyzed in both laboratories, measurements made at WHOI were 1.48‰ lower in δ^{13}C and 0.50‰ higher in δ^{18}O for OM12_07V and 4.28‰ higher in δ^{13}C and 0.95‰ lower in δ^{18}O for OM12_07X2. The source of this discrepancy is unknown, but it suggests that caution should be taken in interpreting small variations in the stable isotope compositions of fresh carbonates along alkaline spring flow paths measured at the University of Waterloo. Regardless, these differences remain small relative to the range of isotopic compositions observed in carbonates formed at hyperalkaline springs in Oman.

The most depleted δ^{18}O and δ^{13}C values are observed in fresh carbonate films on alkaline spring surfaces and in recently-formed preserved travertines (pale blue diamonds and green squares in Figure 5a), but several bottom floc samples also record highly depleted bulk isotopic compositions (dark blue diamonds in Figure 5a). Isotopic depletions are not restricted only to recently-formed samples. Even travertines as old as 40,000 years may preserve significantly depleted isotopic values, e.g., δ^{18}O_{VPDB}~ -13‰ and δ^{13}C_{VPDB}~ -20‰.

Samples at the equilibrium end of the observed δ^{13}C-δ^{18}O trend consist of several old travertines and a few bottom flocs that line hyperalkaline pools. Their isotopic compositions appear to be in equilibrium with the observed range of present-day spring-
water temperatures and δ\(^{18}\)O values and with the carbon isotope composition of soil or atmospheric CO\(_2\) (Table 2 and 4; Neal and Stanger, 1985; Clark et al., 1992; Matter, 2005). Bottom floc samples exhibit slightly lower δ\(^{13}\)C than the older travertines and are thus closer to the expected equilibrium with vegetation-influenced soil CO\(_2\) than atmospheric CO\(_2\) (Clark and Fontes, 1990; Clark et al., 1992). Note however, caution should be taken when interpreting the isotopic composition of older travertines in the context of the present-day conditions in Oman. Although conditions similar to today may have prevailed during many periods in the past, both temperature and δ\(^{18}\)O of meteoric water have varied in Oman over the past 50,000 years (e.g., Burns et al., 2001; Weyhenmeyer et al., 2000). Thus, older travertine samples that appear to be in equilibrium with present-day spring-water conditions could have formed in equilibrium at times when temperature and stable isotope compositions of water were similar to those observed today, or these samples may have formed under isotopic disequilibrium but re-equilibrated isotopically with similar conditions at a later time.

There appears to be a weak correlation between the mineralogy and stable isotope composition in fresh carbonate precipitates, with calcite more abundant in highly fractionated samples and aragonite more abundant in the samples whose isotopic compositions are closer to isotopic equilibrium. The average δ\(^{18}\)O value of fresh carbonate precipitates composed of >90% aragonite (n=3) is only ~2‰ lower than expected equilibrium values for average spring conditions of T=28 ± 4°C, δ\(^{18}\)O\(_{\text{water}}\) = 0.1 ± 1.0‰ SMOW (1 S.D.), while the average δ\(^{18}\)O value of fresh carbonate precipitates composed of >90% calcite (n=3) is ~12‰ lower than expected equilibrium values for these average spring conditions (Kim and O’Neil, 1997; Kim et al., 2007). The average
δ¹⁸O value of fresh carbonate precipitates composed of mixtures of both calcite and aragonite (at least ~20% of each, n=8) is ~8-9‰ lower than expected equilibrium values for these average spring conditions, but mixed samples with higher proportions of calcite do not always have larger deviations from equilibrium.

### 4.3.2 Clumped isotope compositions

Similar to their bulk δ¹⁸O and δ¹³C values, Δ⁴⁷ values in fresh carbonate precipitates and preserved travertines also vary significantly, ranging from enriched values (as high as 0.883‰) to values approaching equilibrium with observed alkaline spring temperatures (e.g., observed Δ⁴⁷ as low as 0.750‰ in fresh precipitates and 0.675‰ in preserved travertines compared to expected equilibrium Δ⁴⁷ values of 0.65-0.75‰ for 17-39 ºC; Ghosh et al., 2006; Dennis et al., 2011). The magnitude of Δ⁴⁷ enrichments observed in our samples, ~0.13-0.23‰ relative to the expected equilibrium, are similar to those observed in carbonates derived from high-pH laboratory precipitation experiments (~0.12-0.25‰, Schmid, 2011; ~0.26-0.31‰, Tang et al., 2014) and in travertines from hyperalkaline springs in Liguria (~0.19-0.24‰, Schmid, 2011).

We note inter-laboratory difference exists in the calibration of clumped isotope thermometers (e.g., Ghosh et al., 2006; Dennis and Schrag, 2010; Zaarur et al., 2013; Defliese et al., 2015; Kluge et al., 2015). In this study, we discuss our results by reference to the equilibrium clumped isotope values predicted by the calibration of Ghosh et al. (2006) as re-calculated in the absolute reference frame by Dennis et al. (2011). We regard this as the most appropriate calibration for our data at this stage because our data have been normalized to the accepted values of the two in-house carbonate standards at
Caltech (section 3.5.3). High $\Delta_{47}$ materials yield higher $\Delta_{47}$ values when analyzed at Caltech than in many other labs (Dennis et al., 2011), consistent with the steepness of the Ghosh et al. (2006) calibration produced at Caltech, which appears to remain valid for a wide variety materials analyzed at Caltech regardless of updated digestion procedures at 90°C (Falk and Kelemen, 2015; Tripati et al., 2015). We therefore consider consistent standard measurements to be a more important factor in choosing an appropriate clumped isotope calibration to apply than acid digestion temperature. More importantly, over the temperature range of spring water in Oman (17-39°C), the expected equilibrium $\Delta_{47}$ values are similar for other existing carbonate clumped isotope calibrations (e.g., Dennis and Schrag, 2010; Zaarur et al., 2013; Defliese et al., 2015; Kluge et al., 2015). The maximum difference in expected equilibrium $\Delta_{47}$ values derived from different calibrations is ~0.03‰, much smaller than the range of $\Delta_{47}$ variations observed in our samples. Therefore, the choice of clumped isotope equilibrium calibration should not affect the conclusion of this study.

Relative to expected equilibrium values at average ambient temperatures and fluid isotopic compositions ($\delta^{18}$O$_{\text{water}} \sim$0‰, $T \sim 28$°C; Table 2), enrichments in $\Delta_{47}$ in fresh carbonate precipitates correlate with depletions in their $\delta^{13}$C and $\delta^{18}$O, yielding a $\Delta_{47}$-$\delta^{18}$O slope of -0.011 between samples furthest from isotopic equilibrium and expected equilibrium values (Figure 5). Crystalline films from alkaline pool surfaces, which show the largest depletions in $\delta^{13}$C and $\delta^{18}$O, record enriched $\Delta_{47}$ values of 0.85 ± 0.01‰ (Figure 5b), about 0.10-0.20‰ higher than expected for the range of temperatures observed in alkaline springs in Oman (~17-39°C: Table 2; Paukert et al., 2012; Chavagnac et al., 2013b). These $\Delta_{47}$ values correspond to unrealistically low apparent
clumped isotope temperatures of ~0°C (Ghosh et al., 2006; Dennis et al., 2011). Similar
disequilibrium isotopic signatures are also observed in some bottom floc samples, with
enriched $\Delta_{47}$ values of 0.773-0.883‰. In contrast, aragonite-rich bottom floc whose $^{13}$C
and $^{18}$O fall within the range of expected equilibrium values for ambient conditions in
Oman record $\Delta_{47}$ values of 0.738-0.758‰ (Figure 5b), corresponding to apparent
clumped isotope temperatures of 17-13°C (Ghosh et al., 2006; Dennis et al., 2011). These
apparent temperatures are slightly lower than the lowest spring temperatures measured
during the winter field seasons, but are consistent with typical winter air temperatures in
Oman (Paukert et al., 2012; Oman Directorate General of Meteorology, 2015).

Clumped isotope compositions of preserved travertines also span a large range of
$\Delta_{47}$ values, from 0.855‰ to 0.675‰, which correspond to apparent clumped isotope
temperatures of -1°C to 33°C (Figure 5c). Similar to their $\delta^{13}$C and $\delta^{18}$O, $\Delta_{47}$ values of
recently-formed travertines (i.e., with calibrated $^{14}$C ages between modern and 305 years)
overlap with those observed in fresh precipitates at the disequilibrium end of the isotopic
trends. Some older travertine subsamples (calibrated $^{14}$C ages of 18,350 - 41,610 years)
also record disequilibrium $\delta^{13}$C, $\delta^{18}$O, and $\Delta_{47}$ values overlapping those observed in
recently-formed travertines, while other travertine subsamples (calibrated $^{14}$C ages of
34,000-45,000 years) record $\delta^{13}$C, $\delta^{18}$O, and $\Delta_{47}$ values between the disequilibrium values
observed in recently-formed travertines and values consistent with equilibrium at
temperatures of ~35°C (Kim and O’Neil, 1997; Ghosh et al., 2006; Dennis et al., 2011).
Note that some subsampled layers in one travertine outcrop (OM10-32) yield $\Delta_{47}$ values
higher than expected from the isotopic trends observed in fresh precipitates. These
additional enrichments are interpreted to reflect mixing between isotopically distinct
generations of carbonate within the travertine layers (see discussion in section 5.1.3).

5. Discussion

5.1 Fresh calcium carbonate precipitates

5.1.1 Disequilibrium end-member

Among different types of fresh carbonate precipitates, surface films record the
greatest extent of stable isotope disequilibrium (e.g., $\delta^{18}$O$_{VPDB} = -16.7\%$, $\delta^{13}$C$_{VPDB} = -$
$27.2\%$, $\Delta_{47} = 0.851\%$), but several bottom floc samples from shallow flow paths along
travertine surfaces also fall close to this end-member. Note, some of these bottom floc
samples may have formed initially as surface films and then settled to the bottom rather
than precipitating in situ.

Under the high pH conditions observed in alkaline springs, CO$_2$ uptake and carbonate
precipitation is very rapid at the air-water interface. O’Neil and Barnes (1971) proposed
that depleted $\delta^{13}$C and $\delta^{18}$O values in travertines from alkaline springs in northern
California result from CO$_2$ diffusion kinetics across the air-water interface. However,
Clark et al. (1992) found this mechanism could not fully explain the kinetic isotope
effects observed in their high-pH carbonate precipitation experiments and suggested
instead that the observed depletions in $\delta^{13}$C and $\delta^{18}$O in alkaline spring carbonates are
related to the CO$_2$ hydroxylation reaction. They concluded that depleted $\delta^{13}$C values in
these carbonates were best explained by a kinetic isotope fractionation on the order of
15\% during hydroxylation, while their depleted $\delta^{18}$O values resulted from unidirectional
reaction of CO$_2$ with hydroxyl ions, which are isotopically lighter than H$_2$O molecules by
~ 40‰ (Green and Taube, 1963). This mechanism was supported by studies of calcite precipitation from high pH solutions (e.g., pH>12, Dietzel et al., 1992; Kosednar-Legenstein et al., 2008), and their estimated carbon isotope fractionation fall within the range from other experimental studies (e.g., 11 to 39‰ over 18-24°C, Zeebe and Wolf-Gladrow, 2001).

Strong depletions in δ\textsuperscript{13}C and δ\textsuperscript{18}O of the surface film samples are accompanied by significant enrichments in their Δ\textsuperscript{47} values. Although the exact mechanism generating these Δ\textsuperscript{47} enrichments cannot be determined from these data alone, it is expected that the CO\textsubscript{2} hydroxylation reaction responsible for depletions in their δ\textsuperscript{13}C and δ\textsuperscript{18}O will also produce kinetic enrichments in their clumped isotope compositions (Appendix A). We obtain a first-order estimate on the clumped isotope composition of the HCO\textsubscript{3}\textsuperscript{-} produced from the CO\textsubscript{2} hydroxylation reaction, assuming isotopic composition of the CO\textsubscript{2} is in equilibrium with water and no kinetic isotope fractionation is associated with CO\textsubscript{2} hydroxylation (i.e. random addition of OH\textsuperscript{-}). Similar assumptions have been employed in previous studies to estimate the oxygen isotope composition of the HCO\textsubscript{3}\textsuperscript{-} derived from this reaction (e.g., Rollion-Bard et al., 2003). Our estimation suggests that, at 300K, CO\textsubscript{2} hydroxylation leads to enriched clumped isotope compositions of HCO\textsubscript{3}\textsuperscript{-} relative to the expected equilibrium values, with a Δ\textsubscript{47}-δ\textsuperscript{18}O slope of -0.012 (See details in Appendix A).

Because CO\textsubscript{2} uptake and carbonate precipitation is rapid at the air-water interface in alkaline springs, there are limited opportunities for oxygen isotope and clumped isotope equilibration of the DIC, especially under those high pH conditions. Therefore, the Δ\textsubscript{47} values of the carbonates precipitated at the surface of alkaline springs are expected to reflect that of the HCO\textsubscript{3}\textsuperscript{-} derived from the CO\textsubscript{2} hydroxylation reaction and be enriched
relative to the expected equilibrium values. The agreement between our theoretically
estimated $\Delta_{47}$-$\delta^{18}$O slope of -0.012 and the $\Delta_{47}$-$\delta^{18}$O slope of -0.011 observed between
surface film samples and values expected in equilibrium with average spring water
conditions ($\delta^{18}$O$_{\text{water}}$ \sim 0‰, T \sim 28°C; Table 2) further supports CO$_2$ hydroxylation as the
main cause of the observed depletions in $\delta^{18}$O and $\delta^{13}$C and enrichments in $\Delta_{47}$ (Figure
5).

5.1.2 Equilibrium end-member

The $\delta^{13}$C, $\delta^{18}$O, and $\Delta_{47}$ values of some bottom floc samples are close to the
equilibrium values expected for conditions observed in Oman alkaline springs and
surface runoff waters. The bottom floc samples with isotopic compositions closest to
expected equilibrium values are rich in aragonite. However, calcite and aragonite cannot
be strictly assigned as disequilibrium and equilibrium end-members respectively because
some surface film samples recording strong disequilibrium isotopic signatures also
contain significant proportions of aragonite. Instead, we suggest that aragonite
precipitation may be favored relative to calcite under conditions where isotopic
equilibrium is also more likely to be achieved.

Chavagnac et al. (2013a) suggest aragonite precipitation may be favored when
surface runoff, containing much higher concentrations of Mg$^{2+}$ and DIC than alkaline
spring water, reacts with alkaline spring water. This could occur either as surface runoff
enters an alkaline pool or when alkaline spring waters seep back into pools that have been
flooded with surface runoff. Increases in the Mg/Ca ratio under these conditions could
favor precipitation of aragonite rather than calcite, and atmospheric- or soil-derived DIC
in the surface runoff could have already equilibrated isotopically before reaction with alkaline fluids, leading to apparent equilibrium values in $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$ of the resulting bottom floc. Thus, the isotopic composition of bottom floc samples that appear close to equilibrium could reflect conditions during infrequent surface runoff events (i.e., rainy days) rather than the observed alkaline spring conditions.

It is however important to note that bottom floc samples could represent mixtures of carbonates formed at different times under varying conditions. They may comprise carbonate precipitated at the bottom of the pool, surface films that have broken and settled to the bottom, or carbonate terraces formed on the edge of the pool that have slumped or been washed into the pool. It is also unknown how long these samples have remained at the bottom of the pool before they were collected. Thus, while we can be fairly certain that surface films formed under the observed conditions at the surface of the pools, the conditions at the time of bottom floc precipitation are not necessarily the same as the conditions measured in the alkaline springs at the time of sample collection.

5.1.3 Mixing between disequilibrium and equilibrium end-members

We note that some bottom floc samples with $\delta^{13}C$ and $\delta^{18}O$ compositions intermediate between the most kinetically fractionated values and equilibrium values have $\Delta_{47}$ values in excess of linear trends between the enriched disequilibrium values observed in surface films and values representing equilibrium with observed water temperatures (Figure 6). This suggests that some bottom floc samples, particularly those formed in larger alkaline pools, may represent mixtures between these two isotopically distinct carbonate end-members.
It is known that mixing of two carbonates with different $\delta^{13}C$ and $\delta^{18}O$ may result in a $\Delta_{47}$ value of the mixture that is not linear with respect to the proportions of the two end-members (Eiler and Schauble, 2004; Affek and Eiler, 2006; Halevy et al., 2011, Defliese and Lohmann, 2015). The exact $\Delta_{47}$ value of the mixture can be higher or lower than the weighted average of the two end-members, depending on the differences in the $\delta^{13}C$ and $\delta^{18}O$ of the two end-members. For two end-members whose $\delta^{13}C$ and $\delta^{18}O$ values are positively correlated, as in carbonates precipitated at alkaline springs, mixing is expected to lead to a positive $\Delta_{47}$ anomaly that is a quadratic function of the mixing ratio and whose magnitude increases with the difference in bulk stable isotope compositions between end-members.

We therefore calculate the expected clumped isotope compositions for mixing between the disequilibrium end-member and several possible equilibrium end-members covering the observed ranges of temperatures in northern Oman, $\delta^{18}O_{water}$ of alkaline spring waters, and $\delta^{13}C$ of soil or atmospheric CO$_2$ (Figure 6, Table 4). These calculations show that the bulk stable isotope and clumped isotope compositions of most bottom floc samples from larger alkaline pools (open blue diamonds in Figure 6) are not consistent with mixing with an end-member that formed under equilibrium with alkaline spring conditions observed at the time of collection. For example, the “Misbit” curve in Figure 6 does not pass through precipitates collected in that spring (black crosses). Instead, their isotopic compositions are better explained by mixing between the disequilibrium end-member and an equilibrium end-member formed at temperatures of about 17-25°C and $\delta^{13}C$ of soil CO$_2$ (Figure 6). While slightly lower than temperatures typically observed in hyperalkaline spring water in Oman, the temperature of this inferred
equilibrium end-member agrees well with average winter air temperatures in northern Oman (e.g., January average daily temperature range of 12-26°C in Nizwa, Oman) and may reflect the temperature of surface runoff from winter rainfall rather than the temperature of groundwater discharge. Northern Oman currently receives most of its rainfall during the winter months. The agreement of average rainy season temperatures with temperatures of the inferred equilibrium end-members suggests that identifying such equilibrium end-members in old travertines formed in similar environments could help constrain the rainy season temperatures in the past.

Note, one aragonite-bearing sample from the bottom of a large alkaline pool in Wadi Sudari (OM09-8COPS) does not fall on the mixing trend of a low-temperature equilibrium end-member, but instead would require an equilibrium end-member formed at ~40°C. While it is possible that this sample reflects a carbonate component formed in isotopic equilibrium with rainwater in warmer months, it may be more likely that this sample formed in a shallow flow path along travertine surfaces near the edge of the pool and later washed or slumped into the pool and thus reflect processes other than carbonate mixing (see discussion in section 5.1.4). The fact that a layered travertine sample collected from the edge of this same pool (OM09-89C) has an isotopic composition extremely close to this sample supports the latter explanation.

5.1.4 Equilibration of DIC

Isotopic variations among many of the fresh precipitates that formed in shallow alkaline spring flows along travertine terraces (filled blue diamonds in Figure 6) cannot
be explained by mixing between the disequilibrium end-member and the low-temperature equilibrium end-member described above. The isotopic composition of these samples lie relatively close to the disequilibrium end-member and do not show obvious curvature in their Δ47-δ13C and Δ47-δ18O trends. If we nevertheless seek to explain the variations in isotopic compositions of these samples by invoking carbonate mixing, the equilibrium end-member carbonate would need to have formed above 35°C. Although such temperatures can be attained in some alkaline springs in Oman, water temperatures measured at the exact collection sites of these specific samples do not exceed 29°C. Furthermore, these samples were found along the bottom of rivulets and small, shallow pools along the surface of travertine terraces; at these locations there is less opportunity for surface runoff to collect and react with alkaline spring water to form equilibrium end-members than at locations where alkaline springs form larger “blue pools” within stream beds.

Instead, we suggest that the isotope compositions of these samples reflect partial isotopic equilibration of DIC in alkaline pools and surface flows, creating apparent linear Δ47-δ13C and Δ47-δ18O trends toward the expected equilibrium values with ambient spring conditions. The carbon isotope compositions of the DIC measured in the Oman alkaline springs support this interpretation. δ13C_DIC in most alkaline springs falls between -13 and -20‰, rather than recording the most extreme kinetic depletions (i.e., δ13C as low as -27.2‰ VPDB in surface films). The lack of positive correlations between δ13C_DIC and the concentration of DIC or Mg2+ (Supplementary Figure S2) suggests these variations in δ13C_DIC are more likely related to gradual equilibration of initially 13C-depleted DIC in the alkaline pools, as opposed to mixing with surface run-off waters which would have
higher concentrations of DIC and $\text{Mg}^{2+}$ and more equilibrated isotopic compositions of DIC. However, we do not observe systematic shifts towards equilibrium values in the isotopic compositions of DIC and carbonate precipitates along individual flow paths (Figure 4). This indicates that the isotope equilibration process does not merely occur incrementally along surface flow paths, but may depend also on other factors which would affect the overall residence time of DIC, such as the rates of $\text{CO}_2$ uptake and carbonate precipitation, water depth, and flow regime.

5.2 Preserved travertines

Laminated travertines with ages ranging from modern to over 40,000 years record many of the same processes recorded by fresh carbonate precipitates at alkaline springs. These include (1) kinetic enrichments in $\Delta_{47}$ accompanying depletions in $\delta^{13}C$ and $\delta^{18}O$, associated with hydroxylation of $\text{CO}_2$; and (2) $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$ values that trend from this kinetic disequilibrium end-member toward equilibrium values, likely reflecting gradual, partial isotopic equilibration of DIC in the alkaline pools and surface flow paths. However, these highly porous travertines may also be subject to continued interaction with surface waters and alkaline spring waters after their original deposition, which could result in additional modification of their isotopic compositions via recrystallization (dissolution and re-precipitation) and/or precipitation of secondary carbonates within the pore space of the travertine.
5.2.1 Inheritance and preservation of kinetic trends

The recently-formed laminated travertine samples analyzed in this study (\(^{14}\)C age ≤305 years, n=4) preserve significant disequilibrium signatures in their \(\delta^{13}\)C, \(\delta^{18}\)O, and \(\Delta_{47}\) values (Figure 5). In these travertine samples, the variations of \(\delta^{13}\)C, \(\delta^{18}\)O, and \(\Delta_{47}\) away from the disequilibrium end-member are similar in slope and extent to the trends attributed to partial equilibration of DIC for fresh precipitates, i.e., trends characteristic of fresh precipitates formed in shallow pools and flow paths along travertine terraces. Unlike fresh precipitates formed at the bottom of larger “blue pools,” none of the recently-formed travertine samples record isotopic compositions close to possible equilibrium values. These four samples may not be representative of all recently-formed travertines and may reflect a sampling bias. Delicately layered recent travertine samples were collected from exposed surfaces of travertine terraces, similar to the environment of fresh precipitates formed in shallow rivulets and small pools along travertine terraces, rather than larger pools within wadi (stream) beds. They are thus more closely tied to the process of carbonate precipitation in shallow surface flows and crusts formed at the air-water interface than to bottom floc in pools which are more influenced by occasional surface runoff. Accordingly, we would expect their isotopic composition to reflect the trends associated with kinetic disequilibrium and partial DIC equilibration rather than the non-linear trends associated with mixing with isotopically equilibrated carbonate end-members.

Several of the older travertine subsamples (20,000 – 40,000 years old) also record \(\delta^{13}\)C, \(\delta^{18}\)O, and \(\Delta_{47}\) values that overlap with the kinetic trends observed in fresh precipitates, demonstrating that disequilibrium clumped isotope signals can be preserved
over these time scales and that the same processes operating in the active system today
are responsible for the formation of extensive fossil travertine terraces. However, the
$\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$ of some older travertine subsamples extend beyond the range
observed in fresh precipitates and recently-formed travertines along the DIC equilibration
trend and closely approach the range of values expected for equilibrium with present-day
ambient conditions in alkaline springs. Note, $\delta^{18}O$ values of meteoric water in Northern
Oman may have been up to 6‰ lower than present-day values during previous
interglacial periods (Burns et al., 2001), and groundwater temperatures may have been
about 6°C cooler during the late Pleistocene (Weyhenmeyer et al., 2000). However, even
taking into account these variations, the isotopic compositions of these carbonate samples
would still appear to be close to equilibrium with paleo-conditions. We suggest isotopic
exchange during post-depositional recrystallization may be responsible for shifting the
isotopic composition of these travertine samples towards equilibrium values, as they
interact with surface- and ground-waters. Most fresh precipitates at alkaline springs
contain at least minor amounts of aragonite, but aragonite is absent from all older
travertine samples. This is consistent with our suggestion that recrystallization occurred
in these older travertine samples and has affected their isotopic compositions.

5.2.2 Mixing with subsequent carbonate precipitates

Based on their $^{14}C$ ages and isotopic compositions, subsampled layers (within a 1
m section) of travertine terrace OM10-32C can be classified into three groups: (1)
subsamples with calibrated $^{14}C$ ages of ~30 ky, whose $\delta^{13}C$-$\delta^{18}O$-$\Delta_{47}$ values fall on the
DIC equilibration trend (n=2, medium red squares in Figure 5); (2) subsamples with
calibrated $^{14}$C ages of ~40 ky, whose $\delta^{13}$C-$\delta^{18}$O-$\Delta_{47}$ values approach equilibrium with present-day ambient conditions ($n=2$, dark red squares in Figure 5); and (3) subsamples with calibrated $^{14}$C ages of ~9-18 ky, whose $\delta^{13}$C-$\delta^{18}$O-$\Delta_{47}$ values deviate significantly from the trends observed in fresh precipitates and recently-formed travertines ($n=3$, pink squares in Figure 5). Although the linear correlation in $\delta^{13}$C and $\delta^{18}$O of these three younger subsamples overlaps with trends in other travertine samples from this and previous studies (Clark and Fontes, 1990; Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014), their enriched $\Delta_{47}$ values at intermediate $\delta^{13}$C and $\delta^{18}$O values are strongly suggestive of mixing of two carbonate end-members. Specifically, these intermediate clumped isotope compositions are consistent with mixing between travertine along the DIC equilibration trend and another carbonate end-member with higher $\delta^{13}$C and $\delta^{18}$O, e.g. later generations of carbonate precipitation within the pore space of the travertine (Figure 7). $^{14}$C data from these subsamples also support this interpretation, with modern carbon fractions ($F_m$) positively correlating with their $\delta^{13}$C and $\delta^{18}$O (Figure 7b). Note, mixing of travertines with a younger carbonate end-member with higher $\delta^{18}$O could generate correlations between $F_m$ and $\delta^{18}$O, but would not necessarily form a perfect linear correlation line because the travertine subsamples are unlikely to all have formed at the same time.

Mixing between a hypothetical end-member ($\delta^{13}$C$_{VPDB}=0\%o$, $\delta^{18}$O$_{VPDB}=3.9\%o$, $\Delta_{47}=0.738\%o$) and travertine lying along the DIC partial equilibration trend near the isotopic composition of OM10-32C-9 ($\delta^{13}$C$_{VPDB}=-18.1\%o$, $\delta^{18}$O$_{VPDB}=-10.3\%o$, $\Delta_{47}=0.787\%o$) accurately reproduces $\delta^{13}$C, $\delta^{18}$O, $\Delta_{47}$ values of all three younger subsamples of OM10-32C when the assumed proportion of the hypothetical end-member in OM10-
32C-8, OM10-32C-10, and OM10-32C is 8%, 43%, and 78%, respectively. This hypothetical end-member was derived by extrapolating the observed $\delta^{18}O$-$\delta^{13}C$ correlation in these subsamples (Figure 7a) to $\delta^{13}C_{\text{carbonate}} = 0\%_\text{VPDB}$ (i.e., the maximum expected equilibrium value based on ambient conditions and carbon sources; Clark et al., 1992), then varying the $\Delta_{47}$ of this end-member to obtain the best fit between the calculated mixing curve and the measured $\Delta_{47}$ values of the travertine subsamples (Figure 7d). This hypothetical end-member is consistent with the isotopic composition of a carbonate formed in isotopic equilibrium with atmospheric $CO_2$ ($\delta^{13}C_{CO_2} \sim -7\%_\text{VPDB}$; Clark et al., 1992) and $\delta^{18}O_{\text{water}} = 5.1\%_\text{VSMOW}$ at 20°C. This could represent a realistic scenario where later generations of carbonates precipitate within the pore space of a travertine as pore-water derived from surface waters and/or alkaline spring waters evaporates.

Our results suggest that clumped isotope measurement can be a valuable tool for identifying these kinds of mixing processes, which cannot be readily identified from bulk stable isotope measurements alone. Furthermore, our results suggest measured $^{14}C$ ages of travertine may reflect not only ages of the initial travertine formation, but also later carbonate precipitation within the pore space. Depending on the age of the later carbonate precipitation, the “true” ages of the above travertine subsamples can be tens of thousands of years older than their measured apparent $^{14}C$ ages and the relative chronology of these subsamples can also change substantially (see details in Appendix B).
5.3 Summary of processes affecting isotopic compositions of carbonates associated with alkaline springs

In summary, the observed $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$ values in fresh carbonate precipitates at alkaline springs and in preserved travertine terraces can be explained by a combination of four main processes (Figure 8).

(1) Hydroxylation of CO$_2$. Uptake of atmospheric CO$_2$ by "Type II" alkaline spring-waters (high pH, extremely low DIC, high [Ca$^+$], low [Mg$^{2+}$]), via rapid CO$_2$ hydroxylation reaction, results in strong depletions in $\delta^{13}C$ and $\delta^{18}O$ and enrichments in $\Delta_{47}$ of carbonates. Relative to expected equilibrium values for average alkaline spring conditions, the typical depletion in $\delta^{13}C$ and enrichment in $\Delta_{47}$ are approximately 1.1‰ and 0.011‰, respectively, for every 1‰ depletion in $\delta^{18}O$. This observed $\Delta_{47}$-$\delta^{18}O$ slope agrees quantitatively with our first-order theoretical estimation about the $\Delta_{47}$-$\delta^{18}O$ correlation associated with CO$_2$ hydroxylation reaction.

(2) Partial equilibration of DIC. Although most of the atmospheric CO$_2$ taken up by alkaline spring water is removed rapidly by the precipitation of calcium carbonate, some amount of DIC may remain in the spring water. This residual DIC may gradually equilibrate isotopically at ambient conditions, producing $\delta^{13}C$-$\delta^{18}O$-$\Delta_{47}$ trends towards the expected equilibrium values and resulting in intermediate isotopic compositions observed in both fresh precipitates in shallow alkaline spring outlets and layered travertines.

(3) Mixing of different carbonate end-members. When surface runoff enters alkaline pools, DIC in these runoff waters, which should already be isotopically equilibrated with ambient surface conditions, allows for the precipitation of calcium
carbonate (mostly aragonite) with equilibrium values of $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$. Bottom floc samples that are a mixture of this runoff-derived carbonate and carbonate formed by direct reaction of atmospheric CO$_2$ with alkaline spring water, define mixing trends that are characterized by positive mixing anomalies in $\Delta_{47}$ and slightly shallower $\delta^{13}C$-$\delta^{18}O$ correlations. The shallower slope of these $\delta^{13}C$-$\delta^{18}O$ correlations reflects greater influence of soil CO$_2$ in surface runoff waters, whose $\delta^{13}C$ is lower than that of atmospheric CO$_2$. (b) Non-linear clumped isotope mixing trends are also evident in subsamples of some older travertine specimen, characterizing the mixing between preserved travertines and later generations of carbonate precipitated within their pore spaces. Although such samples may still lie along the typical travertine $\delta^{13}C$-$\delta^{18}O$ correlations, anomalous enrichments of $\Delta_{47}$ at intermediate $\delta^{13}C$ and $\delta^{18}O$ values are indicative of mixing between isotopically distinct end members.

(4) Recrystallization of preserved travertines. Unlike fresh carbonate precipitates, some preserved travertines record $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$ values close to equilibrium with average conditions in alkaline springs and groundwater in Oman. We suggest that these isotope compositions could have been attained by isotopic exchange during post-depositional recrystallization. Other preserved travertines overlap in isotope composition with recently-formed travertines and fresh carbonate precipitates, suggesting that recrystallization affects some, but not all, older travertine terraces. The extent of this recrystallization process may be controlled by the initial carbonate mineralogy (e.g., replacement of aragonite with calcite) and/or changes in hydrology of the travertine terrace over time (e.g., some portions of travertine terraces will be subject to more post-depositional interaction with water than others).
5.4 Potential applications

The overall trends in δ\(^{13}\)C, δ\(^{18}\)O, and Δ\(_{47}\) discussed above can be applied to distinguish alkaline spring processes from other processes generating correlations in carbonate δ\(^{13}\)C and δ\(^{18}\)O and to identify mixing of different carbonate end-members. Both of these are often not possible when examining the bulk δ\(^{13}\)C, δ\(^{18}\)O compositions of carbonates alone.

5.4.1 Identification of carbonate from subaerial hyperalkaline systems

Correlation between enrichments in Δ\(_{47}\) and depletions in δ\(^{13}\)C and δ\(^{18}\)O could serve as a marker to identify carbonates formed by rapid uptake of CO\(_2\) in subaerial alkaline environments. δ\(^{13}\)C and δ\(^{18}\)O data alone are insufficient for identifying these processes, as δ\(^{13}\)C-δ\(^{18}\)O trends similar in slope and range to those observed in alkaline spring systems can be produced by other processes as well. For example, correlated δ\(^{13}\)C and δ\(^{18}\)O variations are also observed in carbonate cements in conglomerates from Sur, Oman, but are thought to reflect variations in the isotopic composition of surface waters due to past changes in rainfall patterns and vegetation (Burns and Matter, 1995). Because the δ\(^{13}\)C-δ\(^{18}\)O trends in those carbonates are not related to the kinetic processes described here, they would be expected to record equilibrium Δ\(_{47}\) values. Similarly, it might be unclear in some cases whether depletions in carbonate δ\(^{13}\)C and δ\(^{18}\)O are due to kinetic effects associated with uptake of CO\(_2\) in alkaline environments or inherited from dissolution of carbonate bedrock, e.g., calcium carbonates precipitated during weathering of ultramafic mine tailings (Wilson et al., 2009). Clumped isotope analysis could be a
useful diagnostic in these cases. If depletions in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ correlate with enrichments in $\Delta_{47}$, kinetic effects during hydroxylation of CO$_2$ would be indicated.

This same correlation between $\delta^{18}\text{O}$ and $\Delta_{47}$ could also be applied to identify extinct alkaline spring systems in terrestrial and extraterrestrial environments. For example, the slope and magnitude of $\delta^{13}\text{C}$-$\delta^{18}\text{O}$ variations in carbonates in Martian meteorites are similar to that observed in carbonates from terrestrial alkaline springs, and serpentinization-related hyperalkaline systems have been suggested as possible sources of methane generation and carbonate precipitation on Mars (e.g., Niles et al., 2005; Oze and Sharma, 2005; Ehlmann et al., 2010; Etiope et al., 2013). Identification of a $\Delta_{47}$ trend in Martian carbonates similar to trends observed in fresh precipitates and associated travertines in Oman could suggest that hyperalkaline springs were present on the surface of Mars, and may provide further constraints on surface environments on Mars. In one clumped isotope study of Martian carbonates, no such correlation was observed (Halevy et al., 2011). However, as a result of the precious nature of these Martian samples and the challenges to perform the clumped analysis on such small amounts of samples, only a relatively small range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations were observed in the limited number of analyses in that study (7.8‰ and 5.9‰ respectively), which could obscure variations in $\Delta_{47}$ expected from the kinetic trends.

5.4.2 Mixing trends: Identification of carbonate mixing and paleoclimate reconstruction

Due to the non-linear nature of mixing in $\Delta_{47}$, clumped isotope anomalies can be one of the clearest indicators of mixing between carbonates with distinct bulk stable isotopic compositions.
In fresh bottom floc samples from larger alkaline pools, we are able to identify a mixing end-member corresponding to equilibrium with temperatures consistent with winter rainfall in Oman. The laminated travertines analyzed in this study are not likely to have formed under similar conditions as these bottom floc samples, and thus do not reflect the same kind of mixing process. However, it is possible that other travertines in Oman have formed in a pool-bottom environment and would preserve the mixing signatures with an equilibrium end-member recording rainy season conditions. In its current arid climate, Oman receives most of its rainfall in the winter months, but it has experienced wetter climates in the past where rainfall was dominated by the summer monsoon (Clark and Fontes, 1990; Burns et al., 2001; Fleitmann et al., 2003). Carbonate formed in pool bottoms of alkaline springs during those periods could record a mixing end-member in equilibrium with summertime temperatures, allowing identification of major shifts in precipitation patterns that are not available from their bulk stable isotope compositions.

\[ \Delta_{47} \] mixing trends observed in the subsamples of our older travertine samples, reflecting influence of later generations of carbonate precipitation, suggest caution needs to be taken when interpreting \(^{14}\text{C}\) age and paleoclimate data from travertines formed at alkaline spring outlets (Appendix B). The non-linear nature of \(\Delta_{47}\) mixing makes it a valuable tool to identify suites of samples that have been affected by later generations of carbonate precipitation, which is not readily apparent from the \(\delta^{13}\text{C}-\delta^{18}\text{O}\) trends alone. Conversely, travertines whose \(\Delta_{47}\) reflect the same processes observed in fresh precipitates at alkaline springs are likely to provide robust \(^{14}\text{C}\) ages and information about their formation conditions.
6. Conclusions

Carbonates precipitated during atmospheric CO\textsubscript{2} uptake by hyperalkaline springs in Oman record significant enrichments in $\Delta_{47}$ correlated with depletions in $\delta^{13}$C and $\delta^{18}$O. These kinetic isotope effects are the result of hydroxylation of CO\textsubscript{2} under high pH conditions and are best reflected in fresh calcite films formed at the air-water interface.

Partial equilibration of the DIC in alkaline springs may shift the clumped isotope and bulk stable isotopic compositions of some bottom floc samples away from this most fractionated end-member along a trend toward expected equilibrium values. These processes are reflected in both fresh precipitates from alkaline springs and associated preserved travertines, though some older travertines may have experienced isotopic re-equilibration.

Because mixing is nonlinear in $\Delta_{47}$, mixing of two isotopically distinct carbonates can be distinguished from equilibration trends or other processes that can also cause correlated variations in $\delta^{13}$C and $\delta^{18}$O. In fresh bottom floc samples from hyperalkaline springs in Oman, this allows us to identify mixing between the above disequilibrium end-member and possible equilibrium end-members. The nonlinear nature of the clumped isotope signature during mixing also makes it possible to identify travertine samples that may have been affected by later generations of carbonate precipitation within the travertine pore spaces. The presence of such subsequent carbonate precipitates complicates the interpretation of the $^{14}$C age and paleoclimate data from travertines.

Mixed analyses may not be easily identified from $\delta^{18}$O, $\delta^{13}$C, and $^{14}$C trends, whereas
Δ47-δ18O-δ13C trends may show distinctive positive Δ47 anomalies at intermediate δ18O
and δ13C values for samples affected by mixing.

Clumped isotope analysis thus provides a range of details about complex processes occurring during the precipitation and preservation of carbonates at hyperalkaline springs which are not readily apparent from δ18O, δ13C, and 14C data alone.

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Appendix A. Estimation of the oxygen isotope and clumped isotope composition of
HCO$_3^-$ derived from CO$_2$ hydroxylation reaction

The CO$_2$ hydroxylation reaction is ubiquitous in aqueous solutions containing
dissolved inorganic carbon:

$$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$$

In high pH solutions, CO$_2$ hydroxylation is the dominant reaction path by which CO$_2$
converts to HCO$_3^-$ (McConnaughey, 1989). To obtain a first order estimation on the
oxygen isotope and clumped isotope composition of the HCO$_3^-$ derived from CO$_2$
hydroxylation, we assume (1) there is no kinetic isotope fractionation associated with
CO$_2$ hydroxylation, i.e. the addition of OH$^-$ is random, and (2) the isotopic compositions
of both CO$_2$ and OH$^-$ are in equilibrium with water at assumed temperatures (Clark et al.,
1992; Rollion-Bard et al., 2003). We then calculate the abundances of different HCO$_3^-$
isotopologues, by considering the reactions between all 12 stable isotopologues of CO$_2$
and 3 oxygen isotopologues of OH$^-:

$$^{12}\text{C}^{16}\text{O}^{16}\text{O} + {16}\text{OH}^- \rightarrow ^{12}\text{C}^{16}\text{O}^{16}\text{O}^{16}\text{O}^-$$

$$^{12}\text{C}^{16}\text{O}^{16}\text{O} + {17}\text{OH}^- \rightarrow ^{12}\text{C}^{17}\text{O}^{16}\text{O}^-$$

$$^{12}\text{C}^{16}\text{O}^{16}\text{O} + {18}\text{OH}^- \rightarrow ^{12}\text{C}^{18}\text{O}^{16}\text{O}^-$$

......

$$^{13}\text{C}^{16}\text{O}^{16}\text{O} + {16}\text{OH}^- \rightarrow ^{13}\text{C}^{16}\text{O}^{16}\text{O}^-$$

$$^{13}\text{C}^{16}\text{O}^{16}\text{O} + {17}\text{OH}^- \rightarrow ^{13}\text{C}^{17}\text{O}^{16}\text{O}^-$$

$$^{13}\text{C}^{16}\text{O}^{16}\text{O} + {18}\text{OH}^- \rightarrow ^{13}\text{C}^{18}\text{O}^{16}\text{O}^-$$

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The abundances of different CO$_2$ isotopologues at assumed temperatures are calculated following the methodology and algorithms described by Wang et al. (2004).

At 300K, for $\delta^{13}$C$_{CO_2, VPDB} = 0\%$ and $\delta^{18}$O$_{H_2O, VSMOW} = 0\%$, our calculation yields $\delta^{18}$O$_{CO_2, VSMOW} = 41.6\%$, $\delta^{18}$O$_{H_2O, VSMOW} = -37.6\%$ and $\Delta_{47, CO_2} = 0.924\%$

(Brenninkmeijer et al., 1983; Green and Taube, 1963; Wang et al., 2004). Accordingly, the isotopic composition of the HCO$_3^-$ derived from CO$_2$ hydroxylation reaction is estimated to be $\delta^{13}$C$_{HCO_3^-, VPDB} = 0\%$, $\delta^{18}$O$_{HCO_3^-, VSMOW} = 15.2\%$, and $\Delta_{63} = 0.590\%$, where $\Delta_{63}$ denotes the extent of $^{13}$C-$^{18}$O clumping (mostly) in the HCO$_3^-$ and is defined the same way as in Guo et al. (2009). This estimated isotope composition of HCO$_3^-$ is depleted in $^{18}$O but enriched in $\Delta_{63}$, compared to the expected equilibrium isotope composition of HCO$_3^-$ at 300K (i.e., $\delta^{18}$O$_{HCO_3^-, VSMOW} = 30.7\%$, $\Delta_{63} = 0.397\%$; Beck et al., 2005; Hill et al., 2014), with an apparent $\Delta_{63}$-$\delta^{18}$O slope of -0.012. In high pH solutions, CO$_3^{2-}$ comprises a far greater proportion of the DIC pool than HCO$_3^-$, but isotopic equilibration between HCO$_3^-$ and CO$_3^{2-}$ is effectively instantaneous, with an equilibrium $\Delta_{63}$ fractionation of 0.033-0.063‰ (McConnaughey, 1989; Tripati et al., 2015). Therefore, the magnitude of clumped isotope enrichment and $^{18}$O depletion in the total DIC pool will be inherited from the HCO$_3^-$ formed during the hydroxylation reaction. This is expected to lead to an apparent $\Delta_{47}$-$\delta^{18}$O slope of the same magnitude in the carbonate solids derived from CO$_2$ hydroxylation reaction (Section 5.1.1, Guo et al., 2009).
Appendix B. Effects of carbonate mixing on apparent $^{14}$C ages of travertine

Precipitation of later generations of carbonates within the pore space of the travertine (e.g. in preserved travertine terrace OM10-32C), if unaccounted for, can result in significant errors in estimating the true formation ages of travertine samples based on $^{14}$C method (Section 5.2.2). To illustrate this, we calculate possible ranges of “true” ages for the initial formation of travertine OM10-32C subsamples.

We assume that the precipitation of “contaminant” carbonate within the travertine pore space occurred at the same time for all sub-samples and did not incorporate any dead carbon. Under these assumptions, the fraction modern carbon (Fm) of the hypothetical contaminant end-member is constrained by the maximum measured Fm in the travertine subsamples and the minimum possible “true” Fm. In other words, the hypothetical contaminant end-member cannot be older than the most recent travertine subsample, and it cannot be so young that the calculated “true” Fm would be less than zero for any subsample. We then calculate the “true” Fm and corresponding $^{14}$C age of each subsample that would produce their measured apparent ages, using the proportions of hypothetical contaminant carbonates estimated in Section 5.2.2 and shown in Figure 7.

Depending on the assumed value for the Fm of the contaminant end-member, the calculated “true” ages of the travertine can be tens of thousands of years older than their apparent $^{14}$C ages and even relative order of formation for the subsamples can change (Table B.1, Figure B.1). Note, in reality, the contaminant carbonates could have formed over multiple episodes or could have incorporated dead carbon. Therefore, the true ages of the travertine can be even less well-constrained.
References


**Figure Captions**

**Figure 1.** Location of hyperalkaline springs and associated travertine terraces where fresh carbonate precipitates and preserved travertines were sampled in this study (black dots). Samail ophiolite shown in green.

**Figure 2.** Photographs of hyperalkaline spring sampling sites and subsampled travertine terraces. (a) Hyperalkaline blue pools within streambed at Qafeefah. (b) Shallow flow of hyperalkaline fluids along the surface of travertine terraces at Al Bana, flow path sampling of carbonate and spring water at OM12_07V and OM12_07U. (c) Surface film (OM11_07V) and bottom floc (OM11_07U) from Misbit Spring pool. (d) Shallow flow of hyperalkaline fluids along the surface of travertine terraces at Al Hilayw, flow path sampling of spring water at OM12_09AA, OM12_09AB, OM12_09AC and sampling of fresh precipitates (bottom floc) at OM12_09AA. (e) Man-made elevated pool collecting alkaline spring water (OM10-6COPS) at Al Bana travertines. (f) Subsampled travertine terrace from Wadi Uqaybah (OM10-32C subsamples 8, 9, 10, 11).

**Figure 3.** Water data from hyperalkaline springs in Oman. (a) Distribution of water temperatures at multiple sites measured in January (this study; Paukert et al., 2012; Chavagnac et al., 2013b) and measured year-round at a single site (Neal and Stanger, 1985). (b) Correlation between δD and δ¹⁸O of spring water, shown relative to the global meteoric water line (GMWL) (Craig, 1961). (c) Distribution of δ¹⁸O values of
hyperalkaline spring water. (d) Distribution of $\delta^{13}$C values of dissolved inorganic carbon in hyperalkaline springs.

**Figure 4.** Stable isotope variations in spring water and carbonate bottom floc along flow paths at Al Bana, Al Hilayw, Falaj 1, and Falaj 2 travertines. There are no systematic variations in $\delta^{13}$C in spring water DIC (panel A) or carbonate bottom floc (panel C). Spring water $\delta^{18}$O increases with distance along some flow paths (panel B) and is likely the result of evaporation along the flow path, which also results in enrichments in $\delta$D (as shown by the correlation between $\delta$D and $\delta^{18}$O of spring water below the global meteoric water line (GMWL) (Craig, 1961) in panel E). Carbonate $\delta^{18}$O in bottom floc sampled along flow paths (panel D) does not show systematic variation with distance, $\delta^{18}$O$_{\text{water}}$, or water temperature (panel E).

**Figure 5.** Clumped isotope and stable isotope results for fresh precipitates (diamonds) and layered travertines (squares). Dashed boxes indicate the range of expected equilibrium values (Table 4). (a) $\delta^{18}$O and $\delta^{13}$C values of fresh precipitates and layered travertine in this study overlap with values from previous studies of Oman travertines (gray circles; Clark and Fontes, 1990; Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014). $\delta^{18}$O and $\delta^{13}$C of fresh precipitates range from highly depleted values in surface films (pale blue diamonds) to more equilibrium-like values in bottom floc (darker blue diamonds), and preserved travertines span a similar range of stable isotope compositions. (b) Clumped isotope compositions of fresh precipitates from alkaline springs range from enriched $\Delta_{47}$ values associated with depleted $\delta^{18}$O values to
compositions near expected equilibrium values. Layered travertines (gray squares) are shown for reference. (c) Clumped isotope compositions of layered travertines: recently-formed travertines from active hyperalkaline systems (green squares); subsamples of travertine terrace OM10-32C grouped by $^{14}$C age (pink squares <20ky, medium red squares ~30ky, dark red squares ~40ky); subsamples of 40,000 year old travertine terrace OM10-78C (orange squares). Dotted lines in (b) and (c) indicate our first-order theoretical estimation of the $\Delta_{47}$-$\delta^{18}$O slope associated with CO$_2$ hydroxylation (Appendix A).

Figure 6. Mixing trends in fresh precipitates from alkaline springs. Each panel shows $\Delta_{47}$-$\delta^{18}$O mixing trends between the disequilibrium end-member (i.e., surface films) and several possible equilibrium end-members: (a) equilibrium with the lowest $\delta^{13}$C values expected in soil CO$_2$ (carbonate $\delta^{13}$C of -15‰ VPDB; Clark et al., 1992), (b) equilibrium with the atmospheric CO$_2$ (carbonate $\delta^{13}$C of 0‰ VPDB; Clark et al., 1992), (c) equilibrium with the lowest $\delta^{18}$O values observed in alkaline springs in Oman (water $\delta^{18}$O -2.1‰ VSMOW; Neal and Stanger, 1985), (d) equilibrium with the highest $\delta^{18}$O values observed in alkaline springs in Oman (water $\delta^{18}$O 2.5‰ VSMOW; this study). Dashed black boxes indicate the range of expected values at equilibrium (Table 4). The black dotted line shown in all panels represents mixing with an equilibrium end-member corresponding to the temperatures and isotopic compositions of alkaline spring water from Misbit Spring, and does not pass through the data points representing fresh carbonate precipitates from that specific spring (black crosses). Most bottom floc samples from larger pools record $\Delta_{47}$ values in excess of linear trends between the enriched
disequilibrium values observed in surface films and values representing equilibrium with observed water temperatures. These trends are best explained by mixing between a disequilibrium end-member and an end-member formed in equilibrium with somewhat cooler temperatures (e.g., 17-25°C, corresponding to $\Delta_{47}$ values of 0.75-0.71‰) than those typically observed in hyperalkaline springs.

**Figure 7.** Mixing trends in young subsamples of OM10-32C. Trends in $\delta^{18}$O, $\delta^{13}$C, fraction modern carbon, and $\Delta_{47}$ suggest subsamples of the layered travertine terrace OM10-32C with ages <20ky represent mixing of two isotopically distinct carbonate end-members. Sample symbols and dashed boxes denoting equilibrium conditions as in Figure 5. A mixing line (solid black line) between primary travertines with stable isotopic compositions similar to that of OM10-32C-9 and a hypothetical carbonate end-member with higher $\delta^{18}$O and $\delta^{13}$C and lower $\Delta_{47}$ (open black circle) reproduces the $\delta^{18}$O, $\delta^{13}$C, and $\Delta_{47}$ values observed in OM10-32C-8, OM10-32C-10, and OM10-32C when the assumed proportion of the hypothetical endmember in each of these subsample is 8%, 43%, and 78%, respectively (panels A, C, D). Increases in fraction modern carbon would accompany increases in $\delta^{18}$O and $\delta^{13}$C due to mixing, but would not produce perfect correlations, as measured $^{14}$C ages (panel B) are influenced both by mixing with the younger end-member and real differences in primary travertine ages.

**Figure 8.** Processes controlling the stable isotope compositions of carbonates formed at hyperalkaline springs (surface precipitates and bottom floc – gray diamonds, travertines – gray squares) can be distinguished by the $\Delta_{47}$ and $\delta^{18}$O trends they produce (panel A), but largely overlap in $\delta^{18}$O and $\delta^{13}$C trends (panel B). These processes include: (1) CO$_2$
hydroxylation produces enrichments in $\Delta_{47}$ and depletions $\delta^{18}O$ and $\delta^{13}C$ (yellow). (2)

Partial equilibration of DIC in alkaline springs shifts isotopic composition of the resulting carbonates from the disequilibrium end-member towards equilibrium with ambient conditions (blue). (3) Mixing of isotopically distinct carbonate end-members results in mixing anomalies in clumped isotope composition. For example, alkaline pool bottom floc can include mixtures of the high pH disequilibrium end-member and carbonate precipitated in equilibrium with surface runoff (green). Similarly, the mixing between the travertines and subsequent generations of carbonate that precipitate within the pore space of travertines (e.g., from pore waters with $\delta^{18}O$ enriched by evaporation) can also result in mixing anomalies in clumped isotope composition (red). (4) Carbonate recrystallization (dissolution and re-precipitation) and isotopic exchange in older travertines (orange).

**Figure B1.** Calculated “true” ages of travertine subsamples of nOM10-32C versus the assumed age of the hypothetical contaminant carbonate end-member (e.g., later generations of carbonate precipitated within travertine pore space). “Apparent” (measured) $^{14}C$ ages (dotted or dashed lines) are plotted for comparison with the calculated “true” ages (solid lines). The proportions of contaminant carbonate end-member used in the calculation of “true” ages are as calculated in Section 5.2.2 and shown in Figure 7: 8% in OM10-32C-8, 0% in OM10-32C-9, 43% in OM10-32C-10, and 78% OM10-32C-11. Subsamples with significant proportions of the contaminant carbonate end-member may have “true” ages tens of thousands of years older than the apparent $^{14}C$ ages (e.g., OM10-32C-10 and OM10-32C-11). The apparent relative
chronology of the travertine subsamples can also be substantially changed by mixing with later generations of carbonate. For example, the measured apparent $^{14}$C ages suggest OM10-32C-9 is the oldest, followed by sample OM10-32C-8, OM10-32C-10, then OM10-32C-11, but depending on the age of the contaminating end-member, the “true” order of these OM10-32C subsamples could be 10, 9, 11, 8; 10, 9, 8, 11; or 9, 10, 8, 11.
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**Fresh precipitates from alkaline spring flow paths - samples with only $\delta^{13}$C and $\delta^{18}$O analyzed at University of Waterloo**

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Table 1. Surface carbonate samples associated with alkaline springs

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a UTM coordinates in Zone 40Q. Coordinates where both easting and northing end in zero are approximate, estimated to nearest 10 m.
b Calibrated $^{14}$C age, years before present. By convention, "present" = 1950.
c References for $^{14}$C ages: 1 - Kelement et al., 2011; 2 - Paukert et al., 2012; 3 - Falk, 2013; 4 - Mervine et al., 2014
d Major carbonate minerals (> approx 20%), more abundant mineral listed first; Calcite + aragonite indicates roughly equal proportions
e Minor carbonate minerals (< approx 10%)
f References for mineralogy: 1 - Kelement et al., 2011; 2 - Paukert et al., 2012; 3 - Falk, 2013; 4 - Mervine et al., 2014
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<td>Edwin I</td>
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<td>BDL</td>
<td>OM10_01A,2*</td>
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\(^a\) Rows without water sample ID numbers indicate field measurements.

\(^b\) Site names refer to individual pools at alkaline springs, including source pools and pools along flow paths.

\(^c\) Distance from source spring along flow path over travertine surface.

\(^d\) Limits of detection: DIC - 0.02 mmol/L, Ca - 0.04 mmol/L, Mg - 4.10E-03 mmol/L.

\(^e\) Check mark in "Paukert" column indicates that additional water chemistry data for this sample can be found in Paukert et al. (2012).

\(^f\) Carbonate samples listed in this column were collected at the same site as the corresponding water sample, but not necessarily at the same time. Single or double asterisk indicates that the carbonate was collected at the same time as the water sample:

- carbonates with \(\delta^{18}O\) and \(\delta^{13}C\) analyses only (University of Waterloo), ** - carbonates with full clumped isotope analyses (WHOI).
### Table 3. Stable and clumped isotope data in fresh precipitates and travertine deposits

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample Description</th>
<th>Type</th>
<th>Sample</th>
<th>Major carbonate/mineral</th>
<th>n</th>
<th>δ¹³C, ‰ VPDB</th>
<th>δ¹⁸O, ‰ VPDB</th>
<th>Δ⁴⁷, ‰</th>
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<td><strong>Fresh precipitates from alkaline springs - clumped isotope analyses (WHOI)</strong></td>
<td></td>
<td>OM10-6COPS</td>
<td>Bottom floc, man-made</td>
<td>Calcite</td>
<td>7</td>
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<td>-13.98 ± 0.11</td>
<td>0.826 ± 0.005</td>
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<td>Bottom floc, shallow flow</td>
<td>Calcite + aragonite</td>
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<td>Calcite + aragonite</td>
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<td>-13.20 ± 0.09</td>
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<td>Aragonite, calcite</td>
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<td>-4.24 ± 0.09</td>
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All values corrected to carbonate standards for clumped isotope analyses, as described in text.

Reported uncertainties for clumped isotope data are 1-S.E. of replicate measurements.

External precision for bulk stable isotope compositions measured at the University of Waterloo is 0.2‰ (1-S.D.) for δ¹⁸O and 0.1‰ (1-S.D.) for δ¹³C.
Table 4. Possible carbonate mixing end-members for bottom floc

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<th>Water δ&lt;sup&gt;18&lt;/sup&gt;O, ‰&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Carbonate δ&lt;sup&gt;18&lt;/sup&gt;O, ‰</th>
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</table>

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<sup>a</sup> Minimum and maximum temperatures observed in alkaline springs in Oman (17 and 39°C, respectively; Table 2; Paukert et al., 2012; Chavagnac et al., 2013b) are used to define extreme equilibrium end-members. Measured temperature in Misbit Spring in 2010 (water sample OM10_01A).

<sup>b</sup> Expected Δ<sub>47</sub> values (Ghosh et al., 2006) for given equilibrium end-member temperature; measured Δ<sub>47</sub> value in OM11_07V used as representative disequilibrium end-member.

<sup>c</sup> Minimum and maximum δ<sup>18</sup>O values observed in alkaline spring water in Oman (-2.1 and 2.5‰ VSMOW, respectively; Table 2; Neal and Stanger, 1985) used to define extreme equilibrium end-members. Measured spring water δ<sup>18</sup>O in Misbit Spring (OM10_01A).

<sup>d</sup> Expected carbonate δ<sup>18</sup>O in equilibrium with given δ<sup>18</sup>O<sub>water</sub> value and temperature (Kim and O'Neil, 1997). Measured value in OM11_07V used for disequilibrium end-member.

<sup>e</sup> Extreme end-members defined by minimum and maximum expected carbonate δ<sup>13</sup>C in equilibrium with carbon from soil CO<sub>2</sub> and atmospheric CO<sub>2</sub>, respectively. Expected carbonate δ<sup>13</sup>C in equilibrium with soil CO<sub>2</sub> ranges from approximately -15 to -6‰ VPDB, while expected carbonate δ<sup>13</sup>C in equilibrium with soil CO<sub>2</sub> ranges from approximately -3 to 0‰ VPDB (Clark et al., 1992). Measured δ<sup>13</sup>C<sub>DIC</sub> in Misbit Spring (water sample OM10_01A). Measured value in OM11_07V used for disequilibrium end-member.
Table B.1. Calculated "true" ages of travertine subsamples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Type</th>
<th>% Secondary end-member</th>
<th>Measured $^{14}$C Fm</th>
<th>$^{14}$C age</th>
<th>Max. contaminant Fm $^{14}$C age</th>
<th>Min. contaminant Fm $^{14}$C age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypothetical</td>
<td>Contaminating end-member</td>
<td>100</td>
<td></td>
<td></td>
<td>0.462</td>
<td>7100</td>
</tr>
<tr>
<td>OM10-32C-11</td>
<td>Mixed travertine</td>
<td>78.0</td>
<td>0.369</td>
<td>8890</td>
<td>0.040</td>
<td>30140</td>
</tr>
<tr>
<td>OM10-32C-10</td>
<td>Mixed travertine</td>
<td>42.8</td>
<td>0.198</td>
<td>15640</td>
<td>0.000</td>
<td>&gt;50000</td>
</tr>
<tr>
<td>OM10-32C-8</td>
<td>Mixed travertine</td>
<td>8.2</td>
<td>0.153</td>
<td>18350</td>
<td>0.125</td>
<td>20160</td>
</tr>
<tr>
<td>OM10-32C-9</td>
<td>Travertine end-member</td>
<td>0</td>
<td>0.031</td>
<td>32010</td>
<td>0.069</td>
<td>25760</td>
</tr>
</tbody>
</table>
Figure 3.
Figure 4.
Figure 5.

(A) Scatter plot showing the relationship between δ^{13}C, δ^{18}O, and the equilibrium values. Different symbols and colors represent various samples and time periods.

(B) Scatter plot illustrating the δ^{18}O and Δ_{o.r} values. The hydroxylation model is depicted by a dotted line.

(C) Scatter plot depicting the δ^{18}O and Δ_{p.r} values. The hydroxylation model is shown with a dotted line.
Figure 6.
Figure 7.
Figure 8.

A

- Carbonate mixing (bottom floc)
- Carbonate mixing (travertine)
- $\text{CO}_2$ hydroxylation
- DIC equilibration
- Recrystallization

B

- Recrystallization
- DIC equilibration
- Carbonate mixing (travertine)
- Carbonate mixing (bottom floc)
- $\text{CO}_2$ hydroxylation
Figure B.1.
**Supplementary Figure S1.** Variations in hyperalkaline spring water chemistry and stable isotope compositions plotted against $\delta^{13}$C$_{DIC}$. 
Supplementary Figure S2. Variations in hyperalkaline spring water chemistry with distance from the source spring in shallow flows along the surface of travertine terraces.
Supplementary Figure S3. The $\delta^{13}C$ (A) and $\delta^{18}O$ (B) values of fresh carbonate precipitates and preserved travertines obtained by clumped isotope analysis at WHOI are both in excellent agreement with previously reported bulk stable isotope compositions of these samples (Kelemen et al., 2011; Mervine et al., 2014).